VISIT…

Orbitals and Bonding

CHAPTER 3

MASTERING ORGANIC CHEMISTRY

- Assigning Electrons to Atomic Orbitals
- Recognizing Sigma and Pi Bonds
- Using Simple MO Theory to Construct Bonding and Antibonding Molecular Orbitals
- Identifying the Hybridization of Atoms in Molecules
- Identifying the Atomic Orbitals that Overlap to Form Each Molecular Orbital
- Understanding and Using Resonance
- Understanding Molecular Orbital Energies

CHAPTER 1 DESCRIBED a covalent bond as a pair of electrons that is shared between two atoms. The purpose of this chapter is to reexamine bonding in more depth using a model that employs electron orbitals. This model will provide us with a better understanding of bonds and reactivity. The chapter begins with a review of atomic orbitals. Then a model where bonding results from atomic orbitals interacting to form molecular orbitals is discussed. Because resonance is so important in organic chemistry, considerable attention is devoted to this topic. The idea of orbitals can help us understand resonance better. Finally, a number of examples of how to use resonance and when it is important are presented.

Most of the subsequent chapters in this book use simple line structures or skeletal structures to represent molecules, as was done in Chapters 1 and 2. However, you should always have in mind the model that is presented in this chapter so that you can call on it whenever a better picture for bonding is needed to explain an observation.

Much of what is discussed in this chapter should be a review of material that you learned in general chemistry. However, the presentation here concentrates more on the aspects of bonding that are important in organic chemistry.

3.1 ATOMIC ORBITALS

You should recall from your general chemistry course that electrons have some of the properties of waves. Chemists use the equations of wave mechanics to describe these electron waves. Solving these wave equations for an electron moving around the nucleus of an atom gives solutions that lead to a series of **atomic**

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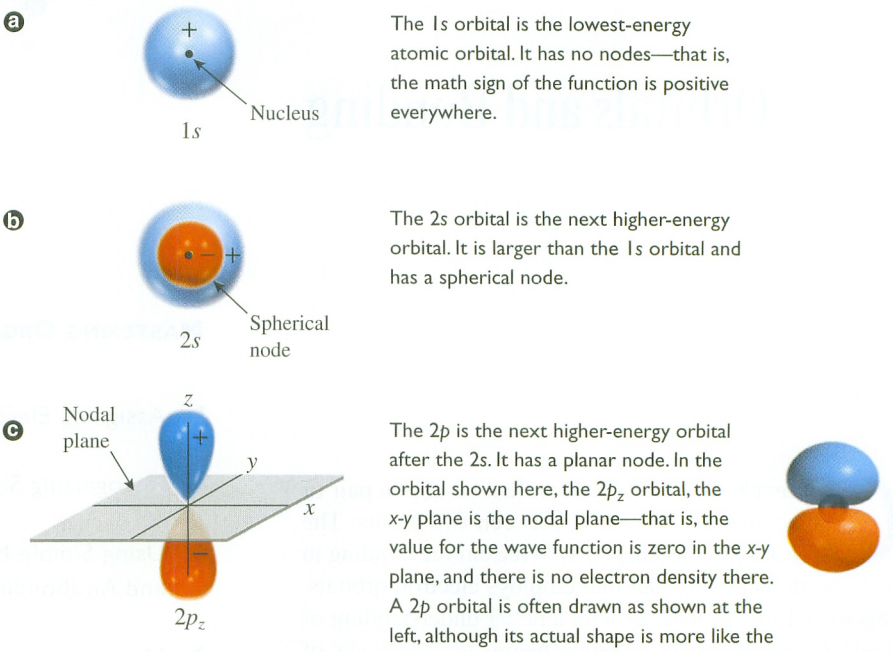

a
+
Nucleus
1s
The 1s orbital is the lowest-energy atomic orbital. It has no nodes—that is, the math sign of the function is positive everywhere.
b
2s
Spherical node
The 2s orbital is the next higher-energy orbital. It is larger than the 1s orbital and has a spherical node.
c
Nodal plane
z
y
x
2pz
The 2p is the next higher-energy orbital after the 2s. It has a planar node. In the orbital shown here, the 2pz orbital, the x-y plane is the nodal plane—that is, the value for the wave function is zero in the x-y plane, and there is no electron density there. A 2p orbital is often drawn as shown at the left, although its actual shape is more like the computer-generated version shown at the right.

Figure 3.1

SHAPES OF ATOMIC ORBITALS: a 1s, b 2s, c 2p.

orbitals. These orbitals describe the location of the electron charge density when an electron occupies that orbital. Another way of stating this is that the shape of the orbital defines a region about the nucleus where, if the orbital contains an electron, the probability of finding that electron is very high. It is simply the space where the electron spends most of its time.

Figure 3.1 shows the shapes of the orbitals that will be of most concern here. The first orbital pictured is the lowest-energy orbital, the **1*s* orbital.** It has a spherical shape, as do all *s* orbitals. Also shown in the figure is the mathematical sign (plus) of the orbital. *This sign does not relate to charge.* It simply indicates that the wave function (the solution to the wave equation) has a positive mathematical value throughout the entire orbital. These math signs are needed when atomic orbitals are combined to make molecular orbitals.

In order of increasing energy the next orbital is the **2*s* orbital.** Like the 1*s* orbital, it has a spherical shape. It is larger than the 1*s* orbital—that is, it extends farther out from the nucleus. Interestingly, the 2*s* orbital has a region where the mathematical sign of the wave function is positive and another region where the sign is negative. It also has a region where the value of the wave function equals zero. Such a region (in this case a spherical surface) is called a **node.** The probability of finding an electron at a particular point is proportional to the square of the value for the wave function at that point. Whether the wave function has a positive or a negative value at that point does not matter, because the square will always be positive. However, the value of the square of the

wave function at a node is zero. This means that the electron density at a node is zero. In general, *the more nodes an orbital contains, the higher energy the orbital is*. Nodes are also very important in molecular orbitals.

The next higher-energy orbital after the 2*s* orbital is the **2*p* orbital,** also shown in Figure 3.1. This orbital is not spherically symmetrical like the *s* orbitals. Its overall shape is something like a dumbbell, with regions of high probability of finding the electron (regions of high electron density) on opposite sides of the nucleus. One lobe of the orbital has a positive math sign and the other has a negative math sign, with a planar node in between. If, as shown in Figure 3.1, the lobes of the orbital are directed along the *z*-axis, then the orbital is called the $2p_z$ orbital and the plane formed by the *x*-axis and the *y*-axis is the plane of the node. There are three 2*p* orbitals, all of the same energy. Orbitals with the same energy are termed *degenerate.* The three 2*p* orbitals are mutually perpendicular. If one is directed along the *z*-axis ($2p_z$), as shown in Figure 3.1, the other two are directed along the *x*-axis and the *y*-axis ($2p_x$ and $2p_y$).

The orbitals pictured in Figure 3.1 are the ones of most interest to organic chemistry, because the atoms that are most commonly encountered in organic compounds are H, C, and other second-period atoms. However, atoms belonging to the third or higher periods of the periodic table are sometimes encountered. Orbitals in the third shell have two nodes. The **3*s*** and **3*p* orbitals** look similar to the 2*s* and 2*p* orbitals except that they are larger and have an additional spherical node. The spherical nodes do not affect the picture for bonding, so 3*s* and 3*p* orbitals (or any other *s* and *p* orbitals) can be treated similarly to 2*s* and 2*p* orbitals when they form molecular orbitals. In addition, the atoms of the third period have **3*d* orbitals** available. We will deal with bonding involving *d* orbitals later, as necessary.

PROBLEM 3.1

Draw a 3*s* atomic orbital and compare it to a 2*s* orbital.

The electron configuration of an atom shows how the electrons are distributed among its orbitals. The electrons are arranged in the orbitals so that the overall energy of the system is minimized. The following set of rules can be used to quickly derive the electron configuration for an atom:

1. Each electron is placed in the lowest-energy orbital available.
2. Each orbital can contain a maximum of two electrons, and these must have opposite spins. This is a result of the **Pauli exclusion principle,** which states that no two electrons can have all four quantum numbers the same. Because two electrons in the same orbital must have three of the quantum numbers the same, the fourth quantum number (the spin quantum number) must be different.
3. When degenerate orbitals are available, the electrons first occupy them singly, with the same (parallel) spins. After all of the degenerate orbitals contain one electron, additional electrons with opposite spins are added to each. This is known as **Hund's rule.**

Figure 3.2 shows the electron configurations for the atoms in the first two rows of the periodic table. This energy level diagram shows the atomic orbitals in order of increasing energy (the lowest-energy orbital is at the bottom) and shows the electrons occupying these orbitals as arrows (the direction of the arrow indicates the spin). This

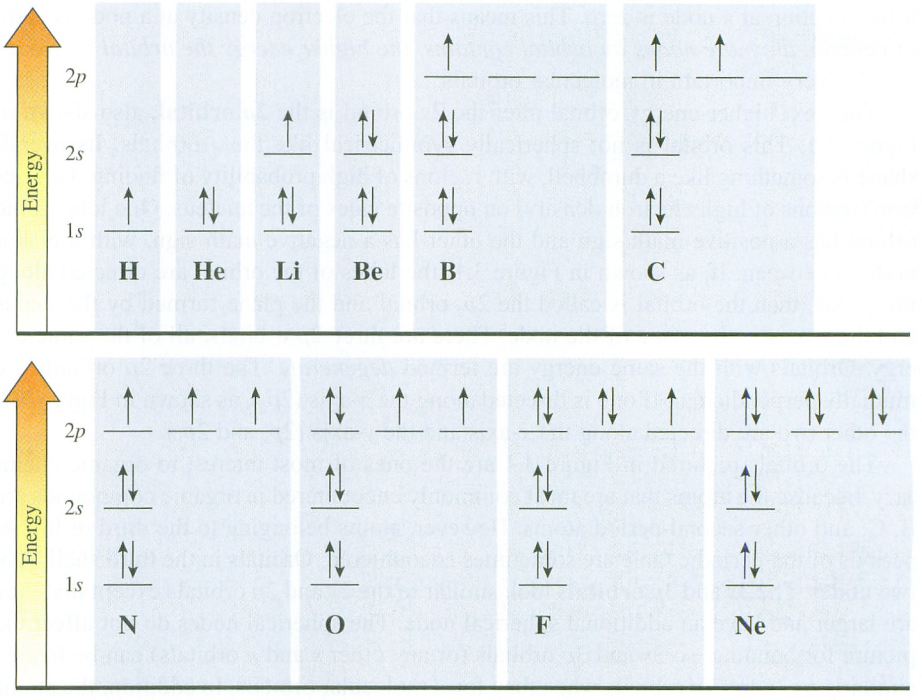


Figure 3.2

ATOMIC ORBITAL ENERGY LEVEL DIAGRAMS. To simplify these diagrams, the orbitals are shown at the same energies for different atoms. Actually, the energy of an orbital decreases as the number of protons in the atom increases. Thus the 2*p* orbitals of fluorine are lower in energy than the 2*p* orbitals of oxygen.

figure can easily be constructed from the preceeding rules. For example, carbon has six electrons. The first two go into the lowest available orbital, the 1*s* orbital (rule 1), with opposite spins (rule 2). Likewise, the next two electrons go into the 2*s* orbital. The last two electrons must be placed in the 2*p* orbitals. Because there are three degenerate 2*p* orbitals, these two electrons are placed in different orbitals, with the same spin (rule 3).

What is the reason behind Hund's rule? Let's consider carbon again. Recall that electrons, having the same charge, repel each other. This electron–electron repulsion is minimized if the electrons are in different regions of space, resulting in a lower-energy situation. If the two electrons in the 2*p* orbitals of carbon have the same spin, they must be in different 2*p* orbitals. (If the electrons were together in the same 2*p* orbital, the Pauli exclusion principle would be violated.) Being in different 2*p* orbitals keeps the electrons in different regions of space.

Figure 3.2 shows the electron configurations for the **ground state** or the **lowest-energy state** for the atoms. Any other electron arrangement is higher in energy and is termed an **excited state.** For example, a carbon atom with two electrons in the 1*s* orbital, one electron in the 2*s* orbital, and three electrons in the 2*p* orbitals is in an excited state. Such an excited carbon atom will exist for only a very short period of time—only until it can find a way to get rid of that extra energy and return the third 2*p* electron to the 2*s* orbital.

PROBLEM 3.2

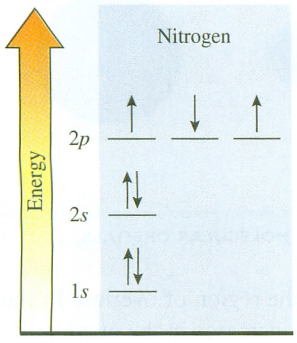
Show an atomic orbital energy level diagram for these atoms:

a) Si **b)** Al **c)** Cl

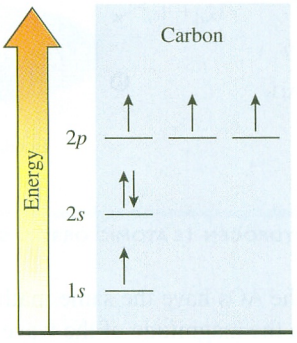
PROBLEM 3.3

Explain whether the electron arrangement for these atoms is the ground state or an excited state:

a)



b)



3.2 MOLECULAR ORBITALS

In isolated atoms the electrons are in the atomic orbitals (AOs) of that atom. What happens to the electrons when atoms come together to form bonds? In the simple Lewis model, some of the electrons are pictured as being shared between atoms. In the orbital model, these shared electrons are pictured as being in orbitals that extend around more than one atom. Such orbitals are called **molecular orbitals** (MOs).

The shapes of the MOs indicate the areas of high electron density in the molecule. MOs are useful in understanding reactions because orbitals must overlap to form any new bond. Thus, MOs help us see how molecules must approach each other for their orbitals to overlap in forming new bonds. Molecular orbitals are especially useful in the discussion of spectroscopy (Chapter 15), aromatic compounds (Chapter 16), and pericyclic reactions (Chapter 22).

Most of what was presented previously about AOs also applies to MOs. The shape of the MO, which describes a region around the nuclei of the bonding atoms where the probability of finding an electron is high, is important, as is the energy of the MO. Let's examine H_2, a very simple molecule, to see what happens.

Let's consider the shape of the MO first. The simplest picture considers molecular orbitals as resulting from the overlap of atomic orbitals. When atoms are separated by their usual bonding distance, their AOs overlap. Where this overlap occurs, either the electron waves reinforce and the electron density increases, or the electron waves cancel and the electron density decreases. The left-hand side of Figure 3.3 shows the overlap of the 1*s* atomic orbitals on two different hydrogens (H_a and H_b) when these hydrogens are separated by their normal bonding distance. The *two* atomic orbitals interact to produce *two* molecular orbitals. The MOs result from a linear combination of the AOs (called the **LCAO approximation**). Simply, this means that the AOs are either added ($1s_a + 1s_b$) or subtracted ($1s_a - 1s_b$) to get the MOs.

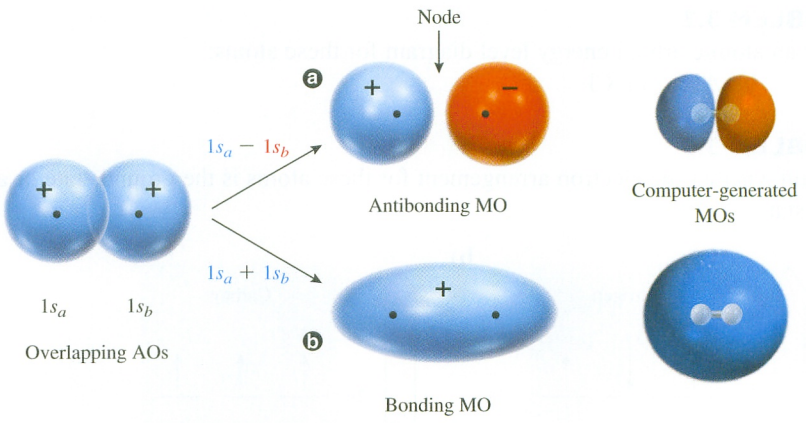


Figure 3.3

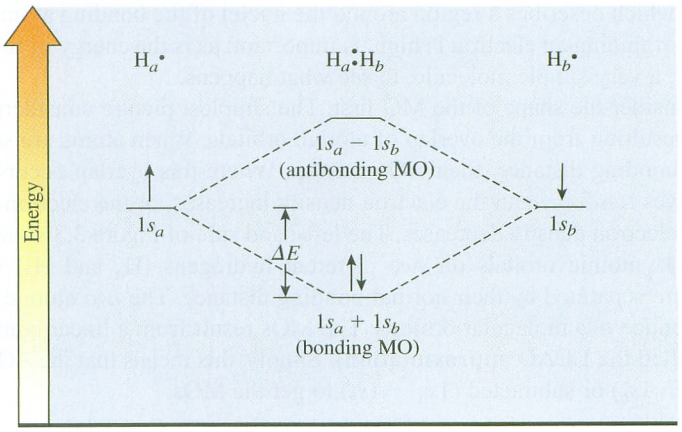
COMBINATION OF HYDROGEN 1S ATOMIC ORBITALS TO FORM MOLECULAR ORBITALS.

In Figure 3.3 the AOs have the same math sign in the region of overlap. In the $1s_a + 1s_b$ combination the magnitude of the wave function increases in the overlap region, and the electron density also increases here. This increase of electron density between the nuclei results in a more stable orbital—the MO is lower in energy than the AOs. Such MOs are called **bonding MOs.** In the $1s_a - 1s_b$ combination the magnitude of the wave function decreases in the region between the nuclei and actually cancels along a plane perpendicular to a line connecting the two nuclei. This results in a node and a decrease in electron density between the nuclei. The resulting MO is less stable than the AOs and is called an **antibonding MO.** In general, the more nodes that are present in a MO, the higher the energy of that MO.

Figure 3.4 shows the energies of these MOs. The energies of the 1*s* AOs of the separated hydrogen atoms are shown on the left and right sides of the diagram. The energies of the MOs are shown in the center of the diagram. The bonding MO is lower in energy than the 1*s* AOs by an amount of energy shown as ΔE in the diagram. In the simple picture we are using, the antibonding MO is higher in energy than the AOs by ΔE also. (A more sophisticated treatment shows that the antibonding MO is actually higher in energy than the 1*s* orbital by more than ΔE.)

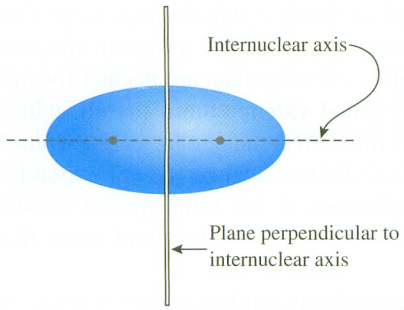
Figure 3.4

ENERGY LEVEL DIAGRAM FOR H_2 MOLECULAR ORBITALS.

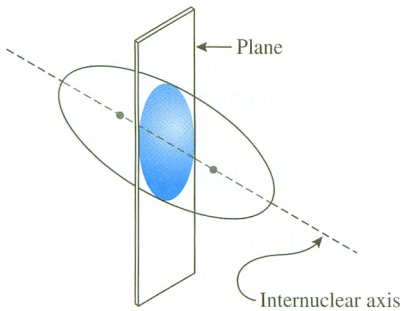


The molecular orbitals are filled with electrons according to the same rules that were used to put electrons in the atomic orbitals of atoms. In this case there are two electrons. These fill the bonding MO. The stability of the molecule is determined by the total energy of the electrons. In the case of H_2 the molecule is more stable than the separated atoms by $2(\Delta E)$. In other words, it would be necessary to add $2(\Delta E)$ of energy to the H_2 molecule to break the covalent bond. As is the case here, the antibonding MOs usually do not have any electrons in them, and they do not affect the energy of the molecule. But they are real and can be occupied by electrons in some situations, such as certain types of spectroscopy and some chemical reactions.

The bond formed between two hydrogen atoms is one example of a **sigma (σ) bond.** In general, the MO of a sigma bond is shaped so that it is symmetrical about the internuclear axis (a line connecting the two nuclei). In other words, if a plane cuts through the MO, perpendicular to a line connecting the nuclei, the intersection of the plane and the MO is a circle. This is shown in Figure 3.5. In a sigma bond, rotation of the AO of one atom of the bond around the internuclear axis does not affect the overlap of the AOs, so it does not affect the energy of the bond.



This view of a sigma MO is perpendicular to a line through the two nuclei—that is, perpendicular to the internuclear axis. A plane that cuts the MO perpendicular to the internuclear axis appears as a line in this perspective.



In this view, the MO is slightly tilted. The plane that cuts the MO perpendicular to the internuclear axis can be seen more clearly.

This is a view down the internuclear axis, perpendicular to the plane that cuts through the MO. In this view it can easily be seen that the intersection of the plane with the MO is symmetrical. Therefore, this is classified as a sigma bond.

Figure 3.5

SEVERAL VIEWS OF A SIGMA BOND.

The MO picture for H_2 agrees completely with the Lewis structure. It shows a pair of electrons shared between the two atoms (in an MO that extends over both atoms), resulting in a molecule that is more stable than the separated atoms. It also explains why the valence for hydrogen is 1. There is no room for additional electrons unless they are placed in the antibonding MO, a destabilizing situation. MO theory can also help us to understand why a molecule such as He_2 does not exist. Like hydrogen, both heliums would use 1*s* AOs to form a bonding and an antibonding MO. However, there would be four electrons to place in these MOs, two from each helium atom. Therefore, both the bonding MO and the antibonding MO would be filled with electrons. The stabilization of the electrons in the bonding MO would be more than offset by the destabilization of the electrons in the antibonding MO. The electrons are actually more stable in the separated atoms.

PROBLEM 3.4

Show an energy level diagram for the MOs for He_2 and show how the electrons would be arranged in these MOs.

What happens with more complicated molecules, which have more than two atoms? To be most accurate, MOs that extend over all the atoms in the molecule should be used. However, such MOs are more complex than are needed for most situations. Instead, we use an approximation called **valence bond theory,** which uses overlap of AOs on the two bonded atoms to form MOs that are localized around these two atoms. These **localized MOs** are much easier to visualize and correspond well to the picture of a bond as a shared pair of electrons. Later, some special situations in which it is necessary to use **delocalized MOs** that extend around more than two atoms will be examined.

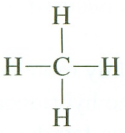
If the approximation that MOs are localized between two atoms is used, then the picture is not as complicated as it might seem. The same thing happens every time. The following generalizations can be made:

1. Two AOs on the bonding atoms overlap to produce two MOs. In more complicated situations the number of MOs produced equals the number of AOs initially involved.
2. The overlapping AOs can be used to approximate the shape of the MOs. One combination of the two AOs results in a lower-energy, bonding MO; the other combination results in a higher-energy, antibonding MO with a node between the nuclei. The math signs are a convenient way to keep track of the nodes.
3. The same rules are used to assign electrons to MOs as are used to assign electrons to AOs. Usually, there are just enough electrons to fill the bonding MOs, and the antibonding MOs remain empty.
4. The bond energy is approximately equal to the total amount of energy by which the electrons are lowered in energy in comparison to the electrons in the AOs—that is, the number of electrons times ΔE.
5. The magnitude of ΔE increases with increasing overlap of the AOs. However, if the atoms get too close together, repulsion between the nuclei starts to dominate and the overall energy increases very rapidly.

By using these rules, we can also analyze more complex situations.

3.3 SINGLE BONDS AND sp^3 HYBRIDIZATION

Let's consider methane (CH_4), a simple organic molecule. First, the Lewis structure, which shows four CH bonds, should be examined.

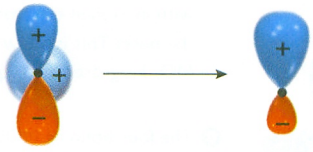


Methane

In the MO picture, there will be a bonding MO (and an antibonding MO) for each bond in the Lewis structure. Furthermore, the MO model must be in accord with experimental observations. Experiments have shown that the bonds in methane are all identical, with tetrahedral geometry. Therefore, methane must have four equivalent bonding MOs, with a tetrahedral arrangement.

Each MO results from an AO on the carbon overlapping with an AO on one of the hydrogens. Only AOs from the valence shell of an atom are used. Each hydrogen uses a 1*s* AO. The four orbitals that are available from the carbon are its 2*s* and three 2*p* AOs. However, problems result if these carbon orbitals are used directly. First, although four equivalent MOs are needed, a MO resulting from a carbon 2*s* AO overlapping with a hydrogen 1*s* AO would obviously be different from a MO resulting from a carbon 2*p* AO overlapping with a hydrogen 1*s* AO. Second, the carbon 2*p* orbitals do not have the correct geometry to point directly at hydrogens that are tetrahedrally arranged around the carbon. This would result in poor overlap between the AOs, a small value for ΔE, and weak bonds.

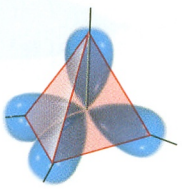
You probably remember the solution to these problems from general chemistry. The 2*s* and the three 2*p* AOs are mathematically combined in a kind of averaging process to produce four equivalent **hybridized AOs.** Because they result from combining one *s* orbital and three *p* orbitals, the new AOs are said to be ***sp*³ hybridized.** The hybrid AOs are ideal for bonding. They are all equivalent, and they have tetrahedral geometry. In addition, each has a large lobe of the orbital pointed in the direction where the other atom of the bond will be and only a small lobe on the other side of the carbon. This directionality of the hybrid AO allows for maximum overlap when it interacts with another AO to form a MO. The hybridization process and the sp^3 hybrid AOs are shown in Figure 3.6.



2*s* and one 2*p* AO

One sp^3 hybrid AO

Part of the 2*s* and part of the 2*p* orbitals are added. Where both AOs are plus, the resulting orbital has a larger lobe. Where the *p* orbital is minus and the *s* orbital is plus, the size of the lobe decreases.



The four sp^3 hybrid AOs point to the corners of a tetrahedron. The small back lobes of the AOs have been omitted for clarity.

Figure 3.6

sp^3 HYBRID ATOMIC ORBITALS.

Important Convention

We are now ready to see how the MOs for methane are formed. The process is just what we have seen before. As shown in Figure 3.7, an sp^3 hybrid AO on carbon overlaps with a 1*s* AO on hydrogen to produce a lower-energy, bonding MO and a higher-energy, antibonding MO. These are both sigma MOs. *(An asterisk is usually used to designate the antibonding MO, as in σ*.)* The two electrons of the bond are found in the bonding MO. An identical process occurs for the other three bonds. The four bonding MOs are pictured in Figure 3.7.

Let's consider ethane, C_2H_6, a slightly more complex example, shown in Figure 3.8. The geometry of the molecule tells the hybridization of the atoms involved. In simple organic compounds, any atom that has tetrahedral geometry will be ***sp*³ hybridized.** Thus, both carbons are sp^3 hybridized in ethane. The CH bonds are formed in the same way as they were in methane. The CC bond is formed by the overlap of sp^3 AOs on each carbon, as shown here.

Overlapping sp^3 AOs — Sigma bonding MO

A similar picture applies to all sigma bonds, even when the atoms have hybridization other than sp^3.

MO pictures for NH_3 and CH_3OH are also shown in Figure 3.8. For ammonia there are four pairs of electrons around the nitrogen—three bonded pairs and one unshared pair—so on the basis of VSEPR theory the geometry of the electron pairs is tetrahedral. (We will not worry about the small deviations from ideal geometries that commonly occur.) Therefore, the hybridization of the nitrogen is sp^3. The MOs for the NH bonds are formed like those for the CH bonds shown earlier. The only difference is the unshared pair of electrons on N. These electrons are in an sp^3-hybridized, nonbonding AO on the nitrogen. In the picture for methanol, note that there are two pairs of electrons in sp^3, nonbonding AOs on oxygen.

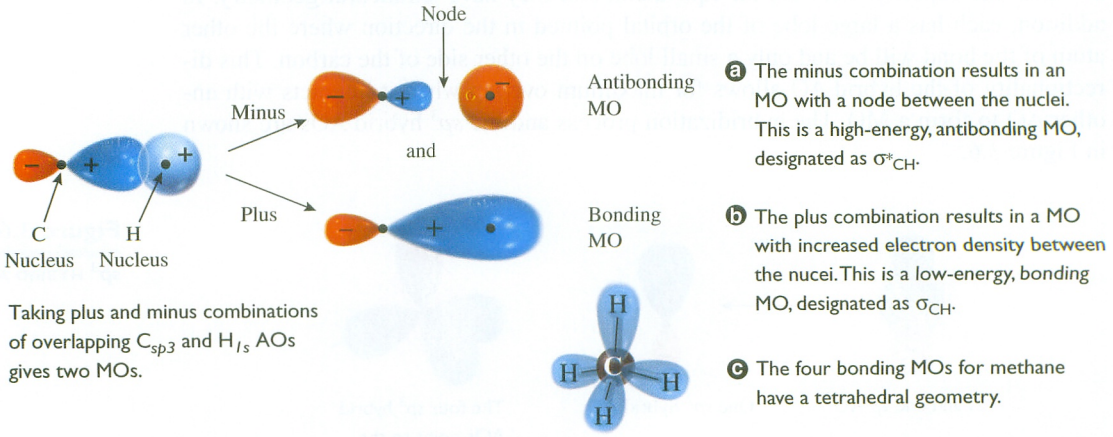
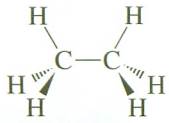

Node
Minus
and
Plus
C
Nucleus
H
Nucleus
Antibonding MO
Bonding MO
H
H
C
H
H
Taking plus and minus combinations of overlapping C_{sp3} and H_{1s} AOs gives two MOs.
a The minus combination results in an MO with a node between the nuclei. This is a high-energy, antibonding MO, designated as σ^*_{CH}.
b The plus combination results in a MO with increased electron density between the nucei. This is a low-energy, bonding MO, designated as σ_{CH}.
c The four bonding MOs for methane have a tetrahedral geometry.

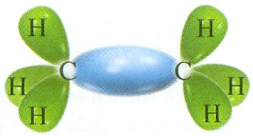
Figure 3.7

ORBITAL PICTURES FOR THE SIGMA BONDS OF METHANE. a Antibonding MO, b bonding MO, and c four bonding MOs.

a



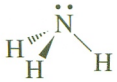
Ethane



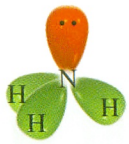
Because each C of ethane has four bonds, the geometry at each is tetrahedral and the hybridization is sp^3.

The CH sigma bond results from a C sp^3 AO overlapping with an H 1*s* AO ($\sigma_{Csp3+H1s}$). The other CH bonds are the same. The CC sigma bond results from the overlap of C sp^3 AOs on both carbons ($\sigma_{Csp3+Csp3}$).

b



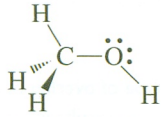
Ammonia



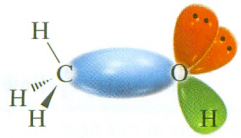
The geometry of the four electron pairs (the three bonding pairs and the unshared pair) of ammonia is tetrahedral, so the hybridization is sp^3.

The unshared pair of electrons is in an sp^3-hybridized, nonbonding AO on the nitrogen. The three NH bonds are $\sigma_{Nsp3+H1s}$.

c



Methanol



The carbon of methanol has four bonding pairs of electrons, so it is tetrahedral and sp^3 hybridized. The geometry of the four electron pairs of oxygen is also tetrahedral, so it is sp^3 hybridized too.

To simplify the drawing, the orbitals for the CH bonds are not shown. They are the same as the CH bonds in ethane. The unshared electrons on the O are in sp^3, nonbonding AOs. The OH bond results from an O sp^3 AO overlapping with an H 1*s* AO ($\sigma_{Osp3+H1s}$). The CO bond results from the overlap of sp^3 AOs on each atom ($\sigma_{Csp3+Osp3}$).

Figure 3.8

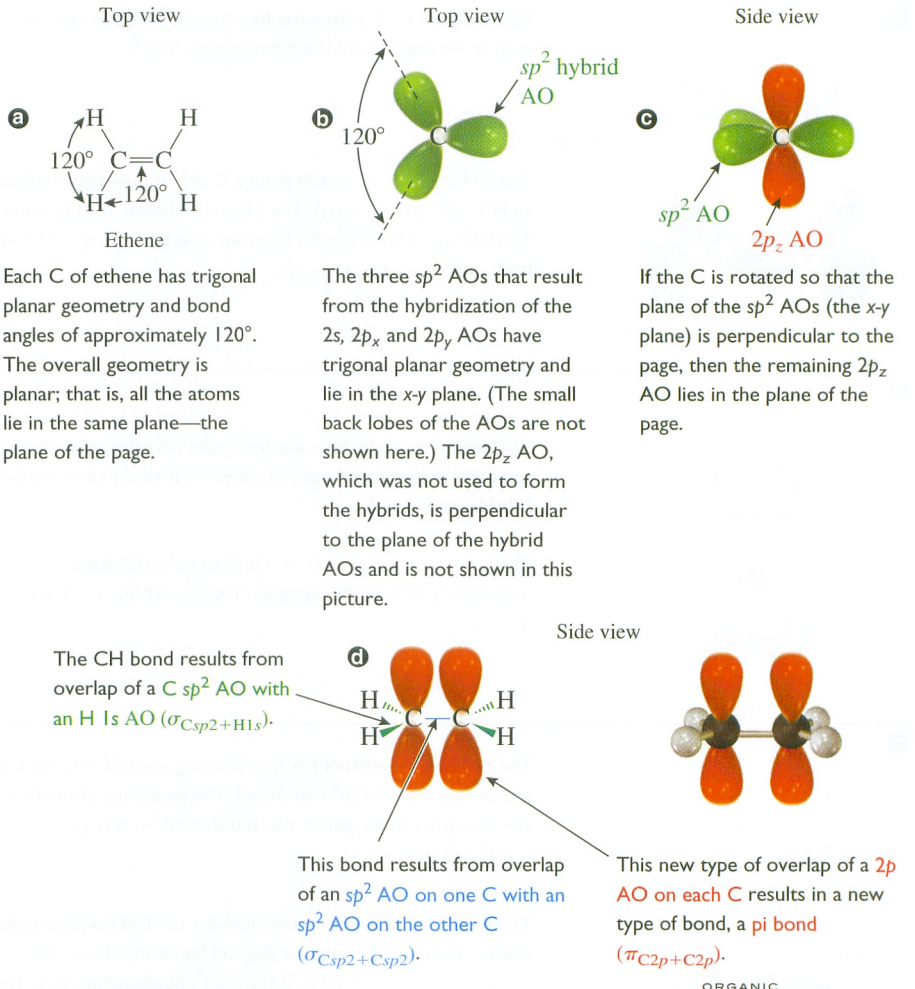
ORBITAL PICTURES FOR THE BONDS OF (a) ETHANE, (b) AMMONIA AND (c) METHANOL. (The small lobes on the back of the various orbitals have been omitted for clarity.)

PROBLEM 3.5

Indicate the type of atomic orbitals that are overlapping to form each of the different kinds of bonds in CH_3OCH_3 (For example, a carbon sp^3 AO and a hydrogen 1*s* AO). What kinds of orbitals are occupied by the unshared electrons on the oxygen?

3.4 DOUBLE BONDS AND sp^2 HYBRIDIZATION

Next, let's see what happens with a compound that has a double bond. A simple organic compound with a double bond is ethene (ethylene), C_2H_4. Again, we should start by looking at the Lewis structure, which is shown in Figure 3.9a. All the atoms of ethene


Top view
Top view
Side view
a
H
H
120°
C=C
H
120°
H
Ethene
b
120°
sp^2 hybrid AO
C
c
C
sp^2 AO
$2p_z$ AO
Each C of ethene has trigonal planar geometry and bond angles of approximately 120°. The overall geometry is planar; that is, all the atoms lie in the same plane—the plane of the page.
The three sp^2 AOs that result from the hybridization of the 2s, $2p_x$ and $2p_y$ AOs have trigonal planar geometry and lie in the x-y plane. (The small back lobes of the AOs are not shown here.) The $2p_z$ AO, which was not used to form the hybrids, is perpendicular to the plane of the hybrid AOs and is not shown in this picture.
If the C is rotated so that the plane of the sp^2 AOs (the x-y plane) is perpendicular to the page, then the remaining $2p_z$ AO lies in the plane of the page.
Side view
The CH bond results from overlap of a C sp^2 AO with an H 1s AO ($\sigma_{Csp2+H1s}$).
d
H
H
C
C
H
H
This bond results from overlap of an sp^2 AO on one C with an sp^2 AO on the other C ($\sigma_{Csp2+Csp2}$).
This new type of overlap of a 2p AO on each C results in a new type of bond, a pi bond ($\pi_{C2p+C2p}$).

Active Figure 3.9 ORGANIC Chemistry Now™

BONDING AND ORBITAL PICTURES FOR ETHENE. Test yourself on the concepts in this figure at **OrganicChemistryNow.**

lie in the same plane. The geometry at each carbon is trigonal planar and the bond angles are approximately 120°. Remember that the MO picture must agree with these experimental observations.

When a compound has a double bond, one of the two bonds is always a sigma bond, formed similarly to the sigma bonds we have already seen. But the second bond is formed in a different fashion. Let's consider the sigma bonds first.

In ethene, each carbon forms three sigma bonds, one to each of the two hydrogens and one to the other carbon. Therefore, three AOs with trigonal planar geometry are needed to form these sigma bonds. This time, the hybrid AOs are formed from the 2*s* and two 2*p* AOs ($2p_x$ and $2p_y$). This results in the formation of three ***sp*²-hybridized AOs.** Each of these AOs has the same general shape as the sp^3 AOs we saw previously; that is, each has a larger lobe of the orbital pointed in one direction and a smaller lobe of the orbital pointed in the opposite direction. The three are equivalent and have trigonal planar geometry, as shown in Figure 3.9b.

Because formation of the sp^2 hybrid AOs used only two of the three $2p$ orbitals, one $2p$ orbital remains: the $2p_z$ AO. The $2p_z$ AO is perpendicular to the sp^2 hybrid AOs. (The sp^2 hybrid AOs lie in the x-y plane because they are formed from the $2p_x$ and $2p_y$ AOs.) All four of the AOs (three sp^2 AOs and one $2p$ AO) are shown in Figure 3.9c.

The MOs for the sigma bonds of ethene are formed by overlap of the AOs in a manner similar to what we have seen before. Each CH bond results from the overlap of an sp^2 hybrid AO on C with a $1s$ AO on H. One of the two CC bonds is a sigma bond and results from the overlap of sp^2 hybrid AOs on each carbon. The second CC bond results from a very different type of overlap involving the unhybridized $2p$ AOs remaining on each carbon. As shown in Figure 3.9d, these orbitals are parallel to each other. They overlap above and below the plane of the atoms, and they overlap less than orbitals that are pointed directly at each other. This new type of overlap, of orbitals that are parallel rather than orbitals that point directly toward each other, results in a new type of bond, called a **pi bond** (π bond).

Figure 3.10 shows this overlap in more detail. The process of forming the MOs is still the same as we saw before. The two AOs overlap. In the plus combination ($2p_a + 2p_b$) the orbitals reinforce in the region above and below nuclei, resulting in a lower-energy, bonding MO. In the minus combination ($2p_a - 2p_b$), the orbitals cancel in the region between the nuclei, a new node is formed, and a higher-energy, antibonding MO results. Because the orbitals are not symmetrical about the internuclear axis, these are not sigma orbitals. Instead, orbitals with this shape are called pi orbitals.

The energies of the pi MOs are shown in Figure 3.11. Note that there are two electrons (the second pair of electrons of the double bond) to put in these MOs. As usual, the bonding MO is filled with electrons, and the antibonding MO is empty. Because the overlap of the p AOs forming the pi MOs is poorer than in the case of AOs forming sigma MOs, ΔE is less for pi MOs than for sigma MOs. Thus, the poorer overlap results in a pi bond being weaker than a sigma bond. From Table 2.1 the bond dissociation energy for a CC single bond is 81 kcal/mol (339 kJ/mol), whereas that for both bonds of a CC double bond is 145 kcal/mol (607 kJ/mol). If it is assumed that the sigma bond of a double bond has approximately the same bond strength as the sigma bond of a single bond, then the approximate strength of a pi bond can be calculated as $145 - 81 = 64$ kcal/mol (268 kJ/mol), considerably less than the strength of a sigma bond.

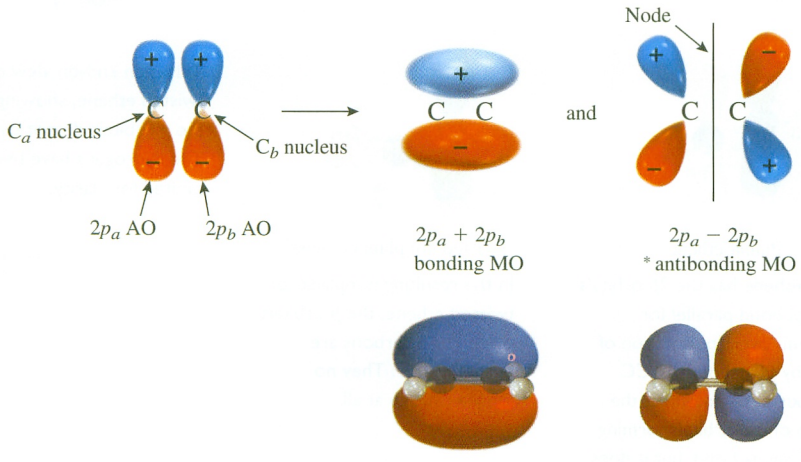
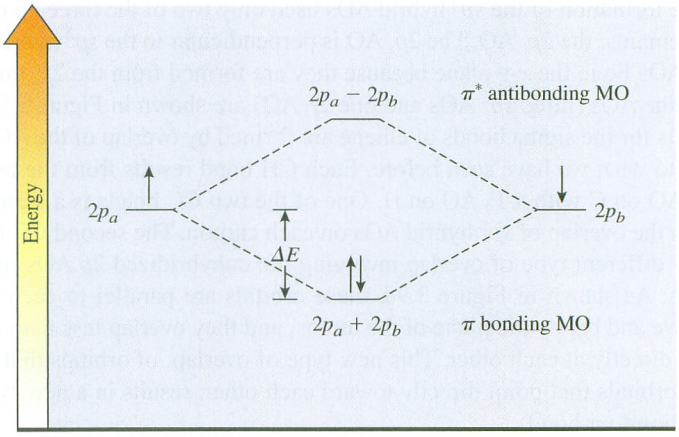


Figure 3.10

FORMATION OF PI BONDING AND PI ANTIBONDING MOLECULAR ORBITALS.

Figure 3.11

ENERGIES OF THE PI BONDING AND ANTIBONDING MOLECULAR ORBITALS.

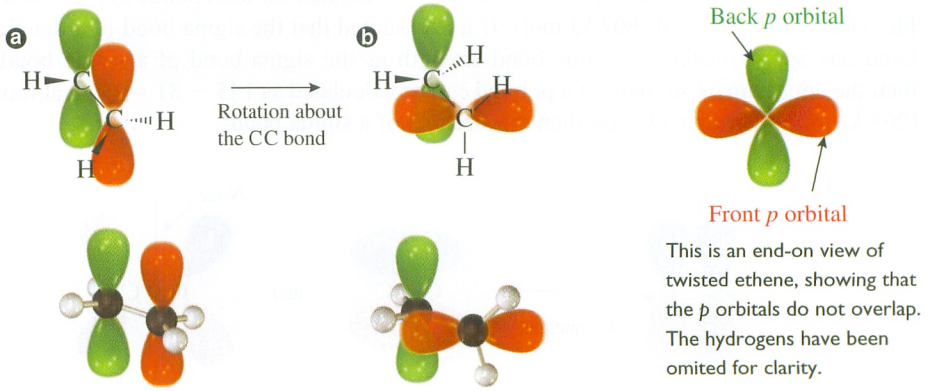


This MO picture helps explain why all the atoms of ethene lie in the same plane. On each carbon the *p* orbital that is used to form the pi bond is perpendicular to the plane defined by the C and the two attached H's. Unless the plane of one C and its two attached H's is the same as the plane of the other C and its two attached H's, the *p* orbitals will not be parallel and overlap will be decreased. As we have seen, as overlap decreases, ΔE decreases and the energy of the electrons increases—the molecule is less stable.

Figure 3.12 illustrates what happens as the plane of one HCH group is rotated relative to the plane of the other HCH group. Figure 3.12a shows planar ethene, with maximum overlap of the *p* orbitals that form the pi bond. If one carbon is rotated 90° about the CC bond, the geometry shown in Figure 3.12b results. This rotation does not change the amount of overlap of the orbitals forming the sigma bond, so its energy is not affected.

Figure 3.12

ROTATION ABOUT THE CARBON–CARBON BOND OF ETHENE.



This is an end-on view of twisted ethene, showing that the *p* orbitals do not overlap. The hydrogens have been omited for clarity.

Planar ethene

Planar ethene has the 2*p* orbitals of the pi bond parallel for maximum overlap. Rotation of one C by 90° about the CC bond axis does not affect the overlap of the orbitals forming the CC sigma bond, but it does affect the overlap of the *p* orbitals forming the pi bond.

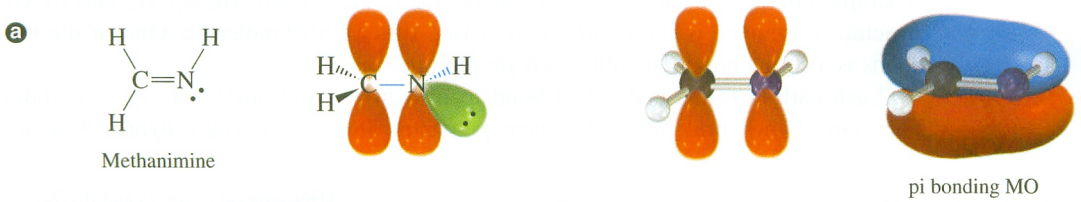
Twisted nonplanar ethene

In the resulting nonplanar or twisted ethene, the *p* orbitals on the two carbons are perpendicular. They no longer overlap at all.

(For this reason a similar rotation about the CC sigma bond of ethane occurs readily.) However, the two *p* orbitals of the pi bond of ethene are now perpendicular. They no longer overlap at all, so ΔE is zero and the pi bond has been broken. Therefore, to cause such a rotation to occur, enough energy must be added to break the pi bond, approximately 64 kcal/mol (268 kJ/mol). At room temperature, only about 20 kcal/mol (84 kJ/mol) of thermal energy is available. Any process that requires more energy than this will not occur at room temperature. So the rotation pictured in Figure 3.12 does not occur.

Simple organic compounds use ***sp*² hybridization** for any atom that has trigonal planar geometry. Consider CH_2NH, shown in Figure 3.13. The geometry at the C is trigonal planar, so it is sp^2 hybridized. It looks just like one of the carbons of ethene. VSEPR theory treats the N as though it has three pairs of electrons in its valence shell (the unshared pair, the pair of the NH bond, and both pairs of the double bond counting as one pair), so the N also has trigonal planar geometry. It looks just like the C but with an electron pair occupying the position of one of the H's. Overall, CH_2NH looks very similar to ethene. The CN double bond is composed of one sigma bond and one pi bond. The geometry is planar, and the CNH bond angle is approximately 120°. The unshared electron pair on N is in an sp^2-hybridized, nonbonding AO.

Figure 3.13 also shows the structure for CH_2O. Because VSEPR theory predicts a trigonal planar geometry for the double bond and the two electron pairs on the oxygen, we will treat it as sp^2 hybridized. Again, the picture is similar to ethene, with one CO sigma bond and one CO pi bond, but with both unshared electron pairs in



In CH_2NH, all the bond angles are approximately 120°, and the molecule has an overall planar geometry. Both the C and the N are sp^2 hybridized. The CH bonds are the same as those in ethene. The NH bond results from an N sp^2 AO overlapping with a H 1s AO ($\sigma_{Nsp2+H1s}$). The unshared electrons are in a nonbonding sp^2 AO on N. The CN sigma bond results from a C sp^2 AO overlapping with a N sp^2 AO ($\sigma_{Csp2+Nsp2}$). The other CN bond is a pi bond resulting from a C 2*p* AO overlapping with a N 2*p* AO ($\pi_{C2p+N2p}$).

In CH_2O, the bond angles are approximately 120°, and the geometry is planar. The C is sp^2 hybridized. The O is also treated as sp^2 hybridized. The two pairs of unshared electrons are each in a nonbonding sp^2 AO on O. The CO sigma bond results from a C sp^2 AO overlapping with an O sp^2 AO ($\sigma_{Csp2+Osp2}$). The other CO bond is a pi bond resulting from a C 2*p* AO overlapping with an O 2*p* AO ($\pi_{C2p+O2p}$).

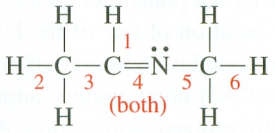
Figure 3.13

ORBITAL PICTURES FOR (a) METHANIMINE, CH_2NH, AND (b) FORMALDEHYDE, CH_2O.

sp^2-hybridized, nonbonding AOs on the oxygen. (Because there are no bond angles involving the doubly bonded oxygen that can be measured, this O could also be treated as unhybridized. In this case the CO σ bond would be formed from an sp^2 hybrid AO on C and a p AO on O, the π bond would still be formed from p orbitals on C and O, and the unshared pairs of electrons would be in $2s$ and $2p$ nonbonding AOs on O. For us there is no real difference between this picture and the previous one, so we will use the hybridized picture in such cases.)

PROBLEM 3.6

What is the hybridization at the N and each C in this molecule? Indicate the type of bond and the orbitals that are overlapping to form it for each of the designated bonds (for example, $\sigma_{Csp3 + H1s}$).



3.5 TRIPLE BONDS AND *sp* HYBRIDIZATION

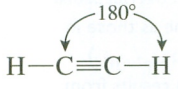
A simple compound with a triple bond is ethyne (acetylene), HC≡CH. The Lewis structure for ethyne is shown in Figure 3.14a. It is a linear molecule. One of the CC bonds is a sigma bond. The other two are pi bonds.

Each carbon forms one sigma bond to a hydrogen and one to the other carbon. Therefore, two hybrid AOs with linear geometry are needed. These hybrid AOs are

Figure 3.14

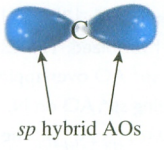
BONDING AND ORBITAL PICTURES FOR ETHYNE. ⓐ Lewis structure, ⓑ two *sp* AOs, ⓒ one sigma and two pi bonds of the triple bond.

ⓐ



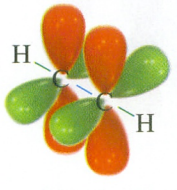
Ethyne is a linear molecule with bond angles of 180°.

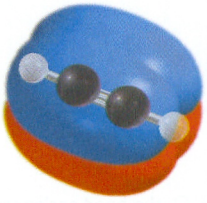
ⓑ



Hybridization of the $2s$ and the $2p_x$ AOs results in the formation of two *sp* hybrid AOs. (The small back lobes of the AOs are not shown here.) The *sp* AOs have linear geometry and have a shape similar to the other hybrid AOs we have encountered. The two unused p orbitals (p_y and p_z) are perpendicular to the hybrid AOs.

ⓒ





Two pi bonding MOs

Each C—H bond results from overlap of a C *sp* hybrid AO with a H 1s AO ($\sigma_{Csp+H1s}$). The C—C sigma bond results from overlap of C *sp* hybrid AOs on each carbon ($\sigma_{Csp+Csp}$). There are two pi bonds (green and red) resulting from a p orbital on one C overlapping with a p orbital on the other C ($\pi_{C2p+C2p}$). The p orbitals of one pi bond are perpendicular to the p orbitals of the other. The three bonds of the triple bond are composed of one sigma bond and two pi bonds.

formed from the 2*s* AO and one 2*p* AO. As shown in Figure 3.14b, the two resulting ***sp*-hybridized AOs** are equivalent and have linear geometry like the 2*p* AO from which they are formed. They have the same general shape as the other hybrid AOs we have seen, with a large lobe pointed in one direction and a small lobe pointed in the opposite direction.

This time there are two 2*p* AOs, perpendicular to the *sp* hybrid AOs, remaining on each carbon. Each of these overlaps with a 2*p* AO on the other carbon to form two pi bonds. These pi bonds are shown in Figure 3.14c. Because the pi bonds are identical, the MOs have the same energies—that is, they are degenerate.

Rotation of one of the carbons about the CC bond axis has no effect on the geometry of the molecule. None of the bond angles is changed. Therefore, we do not have to worry about whether such rotation will occur.

An atom that has **linear geometry** uses *sp*-hybridized AOs to form the MOs. Other examples are considered in problems 3.7 and 3.8.

PROBLEM 3.7

Consider hydrogen cyanide, H—C≡N.

a) What is the hybridization at the N? at the C?

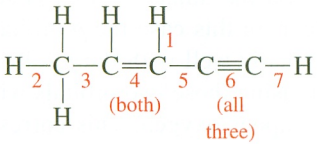
b) What are the types of the three CN bonds? What orbitals are overlapping to form them?

c) In what type of orbital are the unshared electrons on the N?

d) Draw the molecule showing how the orbitals overlap to form the pi bonds.

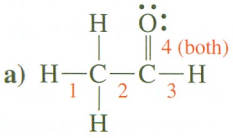
PROBLEM 3.8

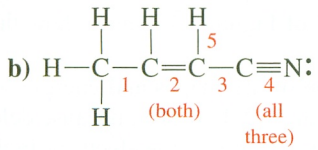
What is the hybridization at each C in this molecule? Indicate the type of bond and the orbitals that are overlapping to form it for each of the designated bonds.

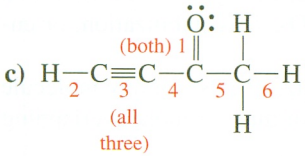


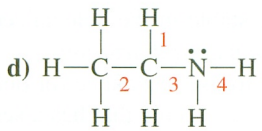
PROBLEM 3.9

Show the hybridization at each of the atoms, except H, in these molecules. Indicate the type of each designated bond and the orbitals that are overlapping to form it.









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3.6 Resonance and MO Theory

In all the cases presented so far, an adequate picture of bonding was obtained by making the approximation that each MO is localized on only two atoms. Sometimes, however, these localized MOs are not a very good model for certain bonds. The situations in which localized MOs fail are the same ones in which normal Lewis structures are inadequate—situations in which resonance is needed to describe the bonding. In such molecules it is convenient to use **delocalized MOs** (MOs that include AOs from more than two atoms) to describe the bonding. In fact, resonance and delocalized MOs are just different ways to describe the same type of bonds. It is not necessary to delve deeply into delocalized MOs, but a brief discussion of them will provide a much better understanding of resonance and when it should be used. As we continue, we will find the resonance picture adequate for most of our discussions.

Let's consider the formate anion, shown in Figure 3.15. The first Lewis structure (a) does not accurately represent the structure of this covalent ion, because a second Lewis structure can be drawn (b) that is equivalent to the first. The actual structure is a resonance hybrid of these two structures. Experiments confirm that the two CO bonds are identical, with a bond length between that of a single and a double bond, and that the charge on each oxygen is the same, approximately $-\frac{1}{2}$.

Figure 3.15c is an attempt to show how the AOs might overlap to form localized MOs in the formate anion. In this localized MO picture, a *p* orbital on the carbon overlaps with a *p* orbital on the upper oxygen to form a pi bond, corresponding to the Lewis structure of Figure 3.15a. In this structure, the lower oxygen has three unshared pairs of electrons. Whenever an atom with an unshared pair of electrons is adjacent to a pi bond, as occurs here, that atom usually assumes a hybridization that places an unshared pair in a *p* orbital because the overlap of this *p* orbital with the *p* orbital of the pi bond on the adjacent atom is stabilizing. It is this overlap that allows resonance to occur. In this case the *p* orbital with the unshared pair on the lower oxygen overlaps equally well with the *p* orbital on the carbon so that the pi bond could also be shown using these two orbitals with an unshared pair of electrons in the *p* orbital on the upper oxygen. This corresponds to the second Lewis structure (b).

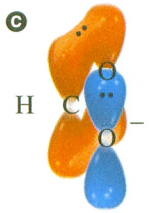
In situations like this one, the overlap of the carbon *p* orbital with one of the oxygen *p* orbitals cannot be ignored as Figure 3.15c attempts to do. Instead, all three *p* orbitals must be used to form MOs that involve the carbon and both oxygens. The three AOs interact to form three delocalized pi MOs. Two of these three delocalized MOs contain the four electrons: the pi electrons and an "unshared pair" of electrons from the localized picture. Part d of Figure 3.15 shows how the orbitals overlap in the delocalized picture.

A detailed discussion of the shapes and energies of delocalized MOs will be postponed until Chapters 16 and 22. However, because delocalization lowers the energies of some of the MOs, the total energy of the electrons in the delocalized MOs is lower than what the total energy of these same electrons would be in the hypothetical localized MOs. The electrons are more stable in the delocalized MOs. This stabilization, or energy lowering, is termed *resonance stabilization.*

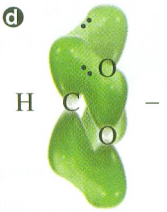
In general, it is necessary to use resonance (or delocalized MOs) for any molecule that is **conjugated,** that is, any molecule that has a series of three or more overlapping

Formate anion

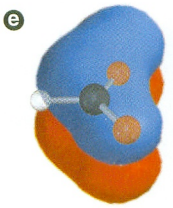
Formate anion is an example of an ion for which two equivalent Lewis structures (a and b) can be drawn. The actual structure is a resonance hybrid of these two structures. Remember to use the double-headed arrow only between resonance structures. Never use equilibrium arrows (⇌) between resonance structures.



This is an attempt to show an orbital picture for the formate anion. It corresponds to the Lewis structure in part a. (The two unshared pairs of electrons on each oxygen that are not involved in resonance have been omitted for clarity.) The two red *p* orbitals overlap to form the pi bond. One unshared pair of electrons is in the blue *p* orbital on the other oxygen. This blue *p* orbital overlaps the red *p* orbital on the carbon just like the red *p* orbital on the other oxygen does.



To get an accurate picture for the formate anion, it is necessary to use delocalized MOs that involve all three of the overlapping *p* orbitals (one from each O and one from C). These three AOs overlap to form three pi MOs. There are four electrons (shown in the Lewis structures in parts a and b as the pi electrons and one unshared pair on oxygen) in these three MOs. This drawing does not attempt to show the shapes of these three MOs, only the orbitals that overlap to form them. More on their energies and shapes will be presented in later chapters.



This is a computer-generated picture of the lowest energy pi bonding MO. The three *p* orbitals overlap without any nodes to produce this MO. It looks much like a pi bonding MO, with electron density above and below the plane of the atoms, except that it extends over three atoms, rather than two. Pictures like *this*, showing the lowest-energy pi MO, are provided throughout the book because they help to visualize how the *p* orbitals overlap to form delocalized MOs.

Figure 3.15

RESONANCE AND ORBITAL PICTURES FOR THE FORMATE ANION.

parallel *p* orbitals on adjacent atoms. The formate anion shown in Figure 3.15 is conjugated because of the three parallel *p* orbitals on the carbon and the two oxygens. However, if the orbitals are not parallel or if there is an extra atom separating them, the overlap is not continuous and the system is not conjugated. Several examples are presented in practice problem 3.1 and problem 3.10.

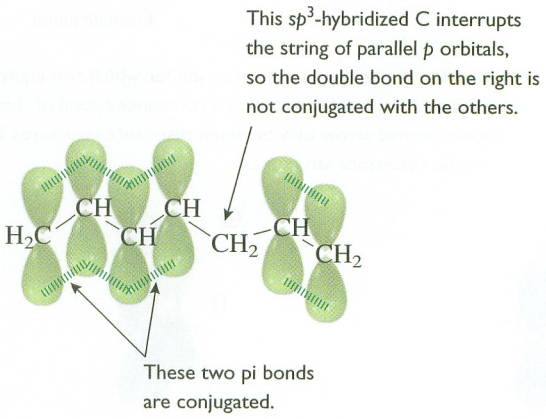
PRACTICE PROBLEM 3.1

Explain which pi bonds are conjugated in this compound:

$$CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH{=}CH_2$$

Solution

The best way to see which bonds are conjugated is to draw the molecule showing the *p* orbitals that form the pi bonds:



PROBLEM 3.10

Circle the conjugated pi bonds, if any, in the following compounds.

a)

b) $CH_3—CH=CH—\overset{\overset{O}{\|}}{C}—CH_3$

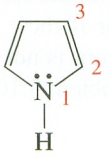
c) $CH_3—CH=CH—C\equiv N$

d) $H—C\equiv C—CH=CH—\overset{\overset{O}{\|}}{C}—H$

e) $CH_3—CH=CH—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$

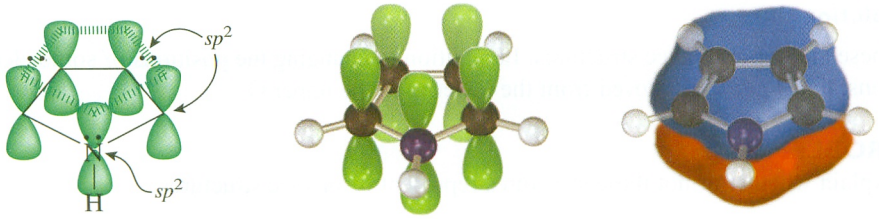
PRACTICE PROBLEM 3.2

What is the hybridization at the indicated atoms in this compound?



Solution

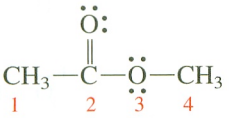
Carbons 2 and 3 are sp^2 hybridized. Nitrogen 1 has an unshared pair of electrons and is adjacent to the pi bonds. Therefore, it is sp^2 hybridized, and the "unshared pair" of electrons is in a *p* orbital. This *p* orbital is conjugated with the *p* orbitals of the pi bonds, resulting in additional resonance stabilization.

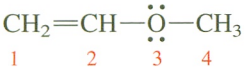


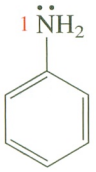
PROBLEM 3.11

What is the hybridization at the indicated atoms in these compounds?

a) $\overset{1}{CH_3}\overset{2}{CH}=\overset{3}{CH}-\overset{4}{NH}-\overset{5}{CH_3}$

b) 

c) 

d) 

3.7 RULES FOR RESONANCE STRUCTURES

Resonance is a very important concept in organic chemistry. It will help us determine how reactive a compound is likely to be and where the most reactive sites in the molecule are located. The following rules will help us to draw resonance structures and determine their importance.

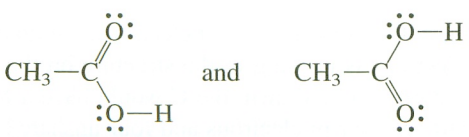
▶ RULE 1

In drawing resonance structures, the nuclei of atoms may not be moved; only pi and nonbonding electrons in conjugated *p* orbitals may be moved.

As we saw for the formate ion in Figure 3.15, resonance structures are just different ways of arranging pi bonds and electrons among a series of adjacent *p* orbitals that form a conjugated system.

PRACTICE PROBLEM 3.3

Explain whether or not these structures represent resonance structures:

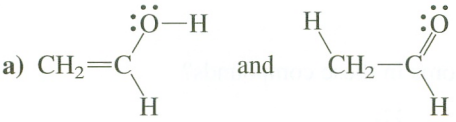


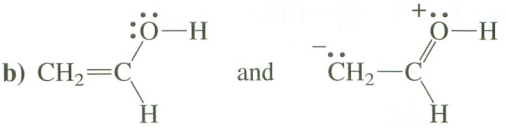
Solution

These are not resonance structures. In addition to changing the positions of some electrons, the H has been moved from the lower O to the upper O.

PROBLEM 3.12

Explain whether or not these structures represent resonance structures:

a)  and

b) 

c) $CH_3CH{=}CH{-}CH_3$ and $CH_3CH_2{-}CH{=}CH_2$

> **RULE 2**
> Each resonance structure must have the same number of electrons and the same total charge.

A common mistake that students make is to lose track of electrons or charges. For example, if one resonance structure is neutral, then any other resonance structure must be neutral overall. It may have formal charges, even if the original structure does not, but each positive formal charge must be balanced by a negative formal charge. To keep the number of electrons the same in each structure, the sum of the pi and the unshared electrons must be the same. Often, but not always, resonance structures have the same number of pi bonds and the same number of unshared electron pairs.

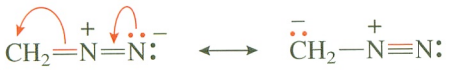
PRACTICE PROBLEM 3.4

Explain why the structure on the right is not a valid resonance structure for the structure on the left.

Solution

The structures do not have the same number of electrons, nor do they have the same total charge. A pair of electrons is missing in the structure on the right, and the formal charge on the C is not correct. (As drawn, the C would have a formal charge of +1.) The structure on the left has four pi electrons and four unshared electrons; the one on

the right has four pi electrons and two unshared electrons. Correct resonance structures are

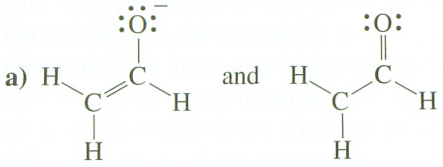


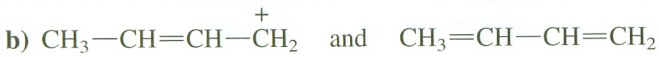
Note how the *curved arrows* are used to help keep track of electrons. *By convention, the arrows always point from where the electrons are in a structure to where they are going in the next structure.* Here the arrows show the electrons of the CN pi bond of the left structure becoming the pair on the C in the right structure and the pair of electrons on the N in the left structure becoming the electrons of the new NN pi bond in the right structure.

Important Convention

PROBLEM 3.13

Explain why the structure on the right is not a valid resonance structure for the structure on the left.

a) 

b) 

c)

d)

RULE 3

The relative stability of resonance structures can be judged by the same rules that were previously introduced to judge the stability of Lewis structures: the octet rule, the number and location of formal charges, and the interactions between charges in the structure.

Because they come closer to satisfying the octet rule, structures with more bonds are usually more stable than structures with fewer bonds. Structures with fewer formal charges are usually more stable because the separation of positive and negative charge requires energy. The location of the formal charges is also important. Structures with formal charges are more stable when unlike charges are closer together and when like

charges are farther apart. Furthermore, it is better to have a negative formal charge on a more electronegative atom and a positive formal charge on a less electronegative atom.

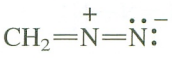
PRACTICE PROBLEM 3.5

Rank the stability of these resonance structures. Describe the actual structure and the amount of resonance stabilization for this compound.

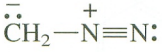
Strategy

First examine the structures to determine whether they satisfy the octet rule. In general, structures that satisfy the octet rule are considerably more stable than structures that do not. In general, structures with more pi bonds are more likely to satisfy the octet rule and are more stable than structures with fewer pi bonds (as long as the octet rule is not exceeded). Next, look at the formal charges in the structures. In general, structures with fewer formal charges are more stable. Other things being equal, it is more stable to have a negative formal charge on a more electronegative atom or a positive formal charge on a less electronegative atom. Finally, remember that like charges repel, so structures that have like charges close together are destabilized. Likewise, opposite charges attract, so structures that have opposite charges farther apart are destabilized.

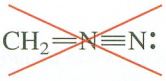
Solution



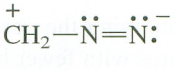
Although it has formal charges, this structure has the octet rule satisfied at all of the atoms. It is the most stable of all of these resonance structures.



This structure also has the octet rule satisfied at all of the atoms. (Note that it has the same number of pi bonds as the previous structure.) It is slightly less stable than the previous one because it has the negative formal charge on the less electronegative C rather than on the more electronegative N.



This structure is extremely unstable because the nitrogen in the center has 10 electrons. As you learned in Chapter 1, structures that have more than 8 electrons around a second-row atom should not be written.



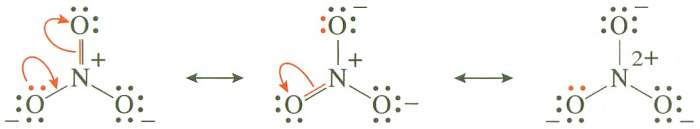
This structure is considerably less stable than the first two because the octet rule is not satisfied at the C. (Note that it has fewer pi bonds than the first two structures.)

The first two structures make important contributions to the resonance hybrid, whereas the contributions of the last two are unimportant, and they are usually not shown. There is more negative charge on the N than on the C because the first structure is somewhat more stable and contributes more to the resonance hybrid. Because it has two important resonance structures, the compound has considerable resonance stabilization and is significantly more stable than is suggested by either of these structures.

PROBLEM 3.14

Rank the stability of these resonance structures.

a) $CH_2{=}CH{-}CH{=}CH_2 \longleftrightarrow {}^{+}CH_2{-}CH{=}CH{-}\ddot{C}H_2^{-}$

b) 

▶ RULE 4

The actual structure most resembles the most stable resonance structure.

In other words, a more stable resonance structure contributes more to the resonance hybrid and is said to be more important. Structures of equal stability contribute equally.

▶ RULE 5

The resonance stabilization energy increases as the number of important resonance structures increases.

For example, if a compound has two equivalent resonance structures, it is considerably more stable than either. We say that it has a large resonance stabilization energy. In contrast, if a compound has two resonance structures but one is considerably more stable than the other, then the structure more closely resembles the more stable (more important) resonance structure. The energy is also close to that of the more stable structure. The compound is only a little more stable than is indicated by the more stable structure, and it has only a small resonance stabilization.

The use of these rules is illustrated by the examples in the following section.

PROBLEM 3.15

Discuss the actual structure and the amount of resonance stabilization for the examples shown in problem 3.14.

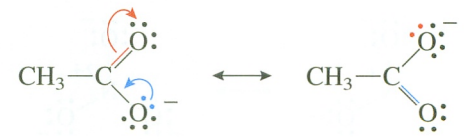
3.8 Types of Resonance Interactions

Figures 3.16 through 3.20 illustrate the common types of bonding situations in which the resonance concept is applied. In each case there is a conjugated series of *p* orbitals. Some of the *p* orbitals are part of pi bonds. Other *p* orbitals may contain a pair of electrons (Figure 3.16), one electron (Figure 3.17), or even no electrons (Figure 3.18). Resonance is also important for pi bonds between atoms of different electronegativities (Figure 3.19) and for cycles of pi bonds (Figure 3.20). The resonance structures are just the various ways the electrons can be arranged among the *p* orbitals to arrive at different but reasonable Lewis structures. As mentioned previously, in most of these examples the resonance structures for a compound have the same number of pi bonds and the same number of unshared electron pairs. However, Figure 3.19 shows a case in which

Figure 3.16

RESONANCE INVOLVING AN UNSHARED PAIR OF ELECTRONS NEXT TO A PI BOND: (a) ACETATE ANION, (b) ACETIC ACID, (c) ACETONE ANION.

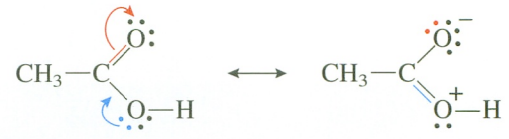
(a)



Acetate anion

This is the acetate anion. The curved arrows are used to help keep track of how electrons are moved to get from the first resonance structure to the second. An unshared pair of electrons on the lower oxygen is moved in to become the pi electrons in the second structure. The pi electrons are moved to become an unshared pair on the upper oxygen. Resonance structures must always have the same total charge — in this case −1. These structures happen to be equivalent in other respects also, so they contribute equally to the resonance hybrid. With two important resonance structures, the acetate anion has a large resonance stabilization. It is significantly more stable than would be predicted on the basis of examination of only one of the structures.

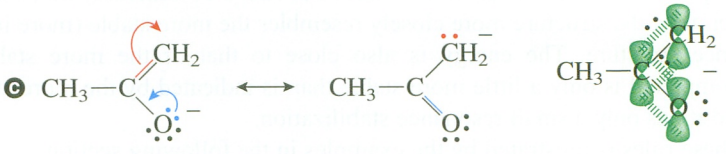
(b)



Acetic acid

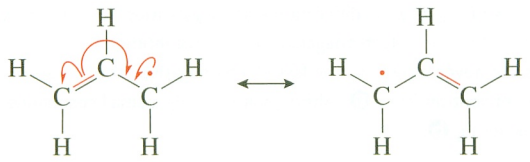
This is acetic acid, a neutral molecule. Similar resonance structures can be written for acetic acid as are shown in part (a) for the acetate anion. In this case the two structures are not the same. The second structure is still neutral overall, but it has two formal charges. Therefore, the first structure is more stable and contributes much more to the resonance hybrid than the second does. Acetic acid has a smaller resonance stabilization than that of acetate anion — it is only a little more stable than the first structure would indicate.

(c)



Anion from acetone

This anion resembles acetate ion, but with a CH_2 in place of one O. Again the same type of resonance structures can be drawn. Both are important, but the first one contributes more because the negative charge is located on the more electronegative oxygen atom. This anion has significant resonance stabilization, though less than the acetate anion. The rightmost diagram shows the conjugated *p* orbitals of this anion.

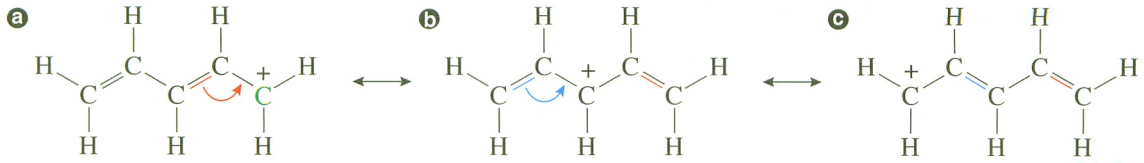


Allyl radical

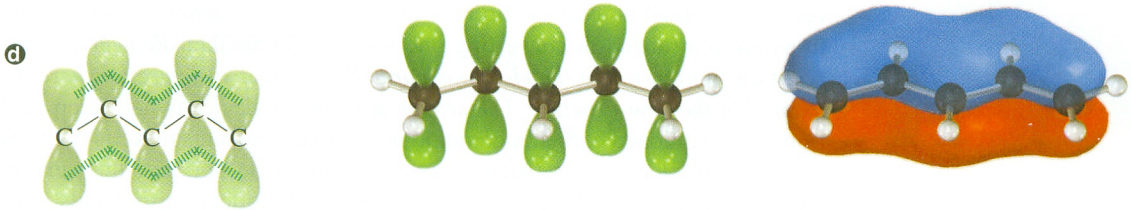
The allyl radical has an odd number of electrons. The odd electron is in a *p* orbital, so the species is conjugated. It has two equally important resonance structures. The octet rule is not satisfied, so this radical is an unstable, reactive species. However, because of its large resonance stabilization, it is not as unstable as would be predicted on the basis of examination of a single structure without delocalization. Single-headed arrows are used to show movement of one electron, rather than electron pairs. Radicals are discussed in more detail in Chapter 21.

Figure 3.17

RESONANCE INVOLVING ONE ELECTRON NEXT TO A PI BOND.



In Lewis structure **a**, the C with the positive charge is sp^2 hybridized with an empty *p* orbital. Therefore, the molecule has a series of five conjugated *p* orbitals, as shown below in **d**. Moving one pair of pi electrons provides **b**, with the positive charge located on the center C. Moving the other pair of pi electrons produces **c**, with the positive charge on the left C. **a** and **c** are completely equivalent, and **b** is quite similar. All three structures are important contributors to the resonance hybrid, and the ion has a large resonance energy. Because the octet rule is not satisfied at one C in any of the structures, this is a reactive species. However, this ion is much less reactive than a similar ion with a positive charge on C but without resonance stabilization. Finally, note that both end carbons and the center carbon have some positive charge and are electron deficient. Reaction with an electron-rich species may occur at any of these three carbons.

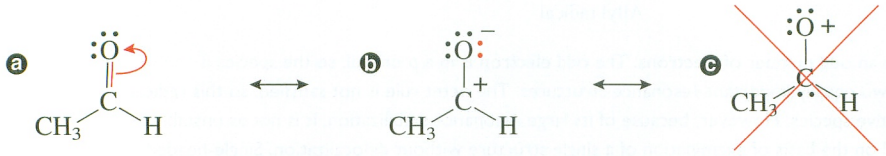


These diagrams show the overlap of a series of five conjugated *p* orbitals in this cation. The hydrogens have been omitted for clarity in the drawing at the left.

Figure 3.18

RESONANCE INVOLVING AN EMPTY *p* ORBITAL NEXT TO PI BONDS.

When a molecule has a pi bond between atoms of significantly different electronegativities, such as carbon and oxygen in this example, a resonance structure where the pi electrons are moved to the more electronegative atom is sometimes shown. (Note that there are only two parallel *p* orbitals involved in this case.) The electrons are never moved to the less electronegative atom, as shown in ⓒ. This compound looks most like ⓐ, with a minor contribution from ⓑ and no contribution from ⓒ. Although it has only a small resonance stabilization, the carbon has more positive charge than would be expected without considering ⓑ.



Ethanal (acetaldehyde)

ⓐ is the most stable resonance structure, and it contributes the most to the resonance hybrid.

Structure ⓑ makes a minor contribution to the resonance hybrid because the octet rule is not satisfied at the carbon. Structures like this one are of significance only when the atoms involved are of different electronegativities.

A resonance structure such as ⓒ, produced by moving the electrons to the less electronegative atom so that there is negative formal charge on the less electronegative atom and a positive formal charge on the more electronegative atom, is not important and should not be shown.

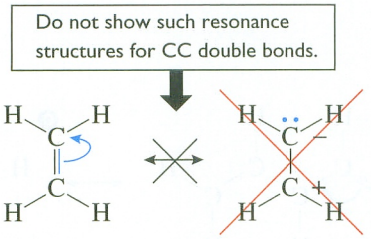
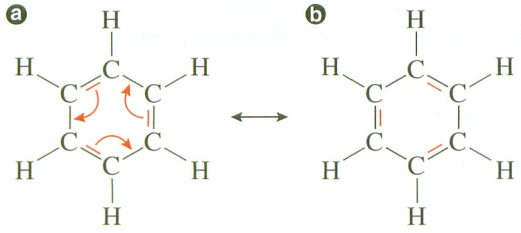


Figure 3.19

RESONANCE INVOLVING PI BONDS BETWEEN ATOMS OF DIFFERENT ELECTRONEGATIVITIES.

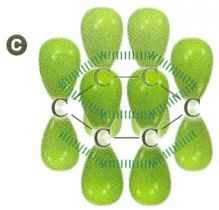
these numbers are not the same. Note that the structures in Figure 3.19 are of very different stability.

Examine these figures carefully so that you gain experience in how and when the resonance model is used. Again note the use of curved arrows to show how the electrons are rearranged in converting one structure to another. *Remember, these arrows point away from where the electrons currently are in a structure to where they will be located in the new structure.* The arrows are a useful device to help keep track of electrons. As mentioned earlier, a common mistake that students make is not being careful enough with electrons so that resonance structures do not have the same number of electrons. The use of the curved arrows and careful attention to details will help you avoid such mistakes. (These arrows will also be used later to show how electrons move in chemical reactions.) Finally, carefully compare the resonance structures in each set to see how their relative importance in contributing to the overall resonance hybrid is determined.

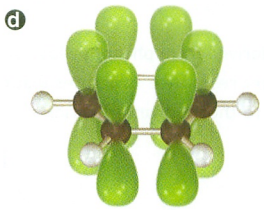


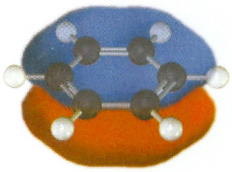
A simple structure for benzene shows a cycle of double bonds. As can be seen in part c, the *p* orbitals of the double bonds form a conjugated series extending completely around the ring. By moving the electrons in a as shown, an equivalent resonance structure is produced, b. Structures a and b make equal contributions to the resonance hybrid. In accord with this, experiments show that all the CC bonds of benzene are identical, with lengths of 1.40 Å, longer than typical double bond (1.34 Å) and shorter than a typical single bond (1.54 Å). Benzene has a very large resonance energy.

Molecules like this, with a ring of parallel *p* orbitals forming a conjugated cycle, are special and often have more stabilization than expected. Chapter 16 treats such molecules in more detail.



Part c shows how the *p* orbitals of the pi bonds of benzene overlap in a complete cycle around the ring. The hydrogens have been omitted for clarity. Another version is shown in part d.





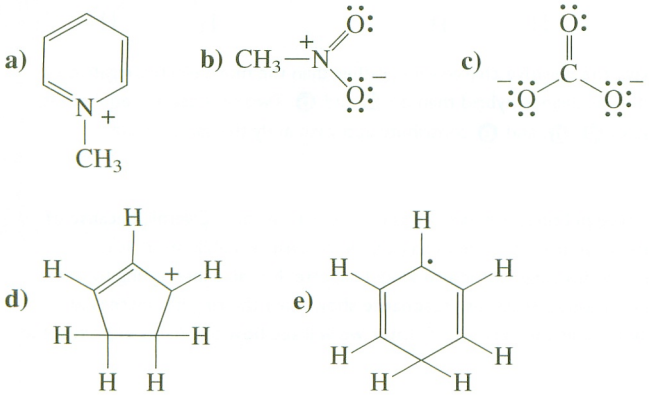
This computer-generated picture, of the lowest-energy pi MO of benzene shows how the *p* orbitals overlap to form a continous cloud of electron density above and below the plane of the atoms in the ring. This is the lowest-energy pi MO because there is no new node introduced when the *p* orbitals overlap.

Figure 3.20

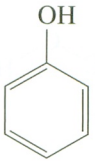
RESONANCE INVOLVING A CYCLE OF DOUBLE BONDS.

PROBLEM 3.16

Show the important resonance structures for these species. Use the curved arrow convention to show how the electrons are moved to create each new resonance structure.



Many compounds involve combinations of the preceding resonance types. Figure 3.21 shows resonance structures for the anion that results from removing a proton (H^+) from the oxygen of phenol.

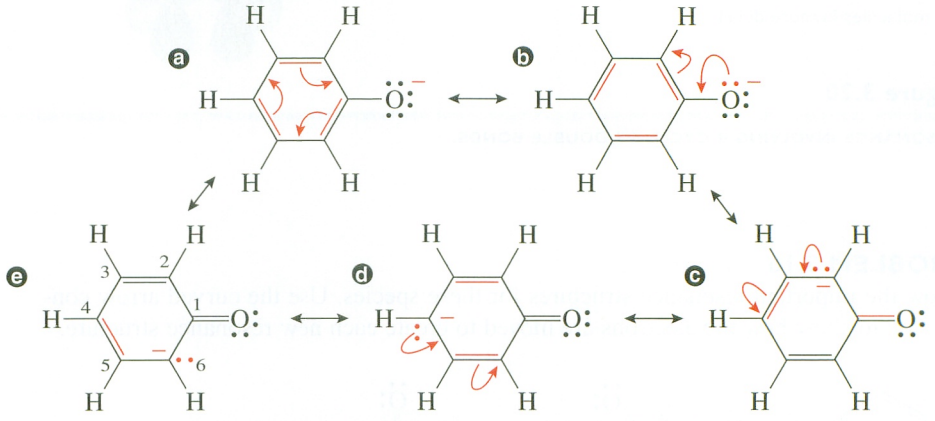


Phenol

This ion has a combination of an unshared pair of electrons (on the O) next to a cycle of double bonds in a benzene ring. The resonance structures are a combination of the types shown in Figures 3.16 and 3.20. The ion has five important resonance structures and thus a large resonance stabilization. Furthermore, the oxygen has decreased electron density in comparison to what might be expected without considering resonance. Certain ring atoms have increased electron density. Later, we will see how these resonance structures accurately predict the chemical behavior of this anion.

The anion derived from phenol by loss of a proton has five important resonance structures that contribute significantly to the resonance hybrid.

Resonance structures ⓐ and ⓑ are equivalent. Both of these contribute equally to the resonance hybrid.



Resonance structures ⓒ, ⓓ, and ⓔ have the negative charge on C rather than the more electronegative O. For this reason they contribute less to the resonance hybrid than do ⓐ and ⓑ. Two of these are equivalent, and the other is quite similar in stability, so ⓒ, ⓓ, and ⓔ contribute approximately the same to the resonance hybrid.

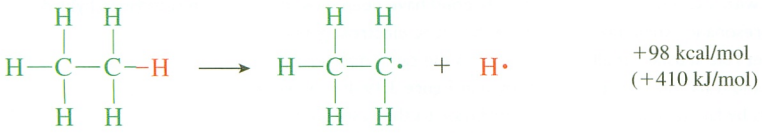
All of these resonance structures have three pi bonds and three unshared electron pairs. Overall, because of the large number of important resonance structures, this anion has a large resonance stabilization. It is significantly more stable than examination of any single structure would indicate. It is also interesting to note the position of the negative charge in the various structures. Resonance shows that the ring has increased electron density at carbons 2, 4, and 6 but not at carbons 3 or 5. Later we will see how this helps explain some experimental results.

Figure 3.21

RESONANCE STRUCTURES FOR THE ANION DERIVED FROM PHENOL.

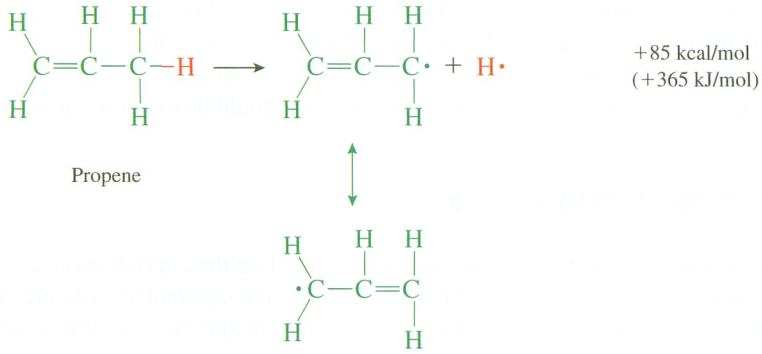
Figure 3.17 shows two equivalent resonance structures for the allyl radical. According to rule 5, this radical should have considerable resonance stabilization. Although it is still an unstable species because the octet rule is not satisfied at one of the carbons, it is considerably more stable than a radical that has no resonance stabilization.

This extra stabilization can be demonstrated by examination of bond dissociation energies. Section 2.2 lists the bond dissociation energy of a CH bond of ethane as 98 kcal/mol (410 kJ/mol). This is the energy that must be added to ethane to homolytically break one of its CH bonds.



Ethane

At first glance, it might seem that a similar amount of energy should be required to break one of the bonds between a hydrogen and the sp^3-hybridized carbon of propene. (Of course, a different bond dissociation energy is expected for the bond between a hydrogen and the sp^2-hybridized carbon.) However, breaking this CH bond requires the addition of only 85 kcal/mol (356 kJ/mol) of energy. It is weaker than the CH bond of ethane by 13 kcal/mol (54 kJ/mol).



Propene

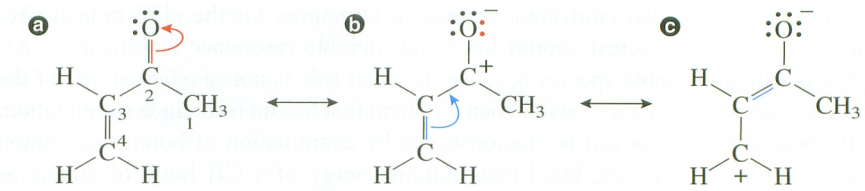
Allyl radical

The CH bond in propene is weaker than the CH bond of ethane because the allyl radical is stabilized by resonance. The ethyl radical has no such resonance stabilization. The difference between these bond dissociation energies provides an estimate of the resonance stabilization of the allyl radical: 13 kcal/mol (54 kJ/mol).

Figure 3.22 shows resonance structures for a compound that has a CO double bond in conjugation with a CC double bond. The resonance structures are a combination of the types in Figures 3.18 and 3.19. Structure (a) has the octet rule satisfied at all atoms and has no formal charges, so it is more stable than the others and contributes the most to the resonance hybrid. Therefore, the actual structure most resembles this resonance structure (rule 4). In addition, the actual energy of the compound is also closer to the energy of the most important resonance structure. In other words, this compound has only a small resonance stabilization. However, even though structures (b) and (c) make

Figure 3.22

RESONANCE STRUCTURES FOR 3-BUTEN-2-ONE.



a has a CC double bond conjugated with a CO double bond. This resonance structure has the octet rule satisfied at all the atoms, and it has no formal charges. It is by far the major contributor to the resonance hybrid.

In **b** the electrons of the CO double bond have been moved onto the more electronegative oxygen in the same manner as shown in Figure 3.19. It is a minor contributor to the resonance hybrid because it has fewer pi bonds and the C has only six electrons.

c is also a minor contributor to the resonance hybrid.

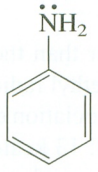
3-Buten-2-one has a small resonance stabilization. It looks most like structure **a**. Interestingly, the resonance structures show that both carbon 2 and carbon 4 are electron deficient. Later, a confirmation of this in the chemical behavior of this compound will be presented.

only minor contributions to the resonance hybrid, they are important because it is these structures that show that carbons 2 and 4 are electron deficient. The electron-deficient nature of these carbons controls the chemical reactions of this compound.

Remember that the individual resonance structures have no discrete existence. The real structure, the resonance hybrid, is a static structure that is an average of the various resonance structures. The two-headed arrow (⟷) should be used only for resonance.

PRACTICE PROBLEM 3.6

Draw the important resonance structures for aniline. Use the curved arrow convention to show how the electrons are moved to create each new resonance structure. Discuss the relative contribution of each to the resonance hybrid and the overall resonance stabilization of the compound.



Aniline

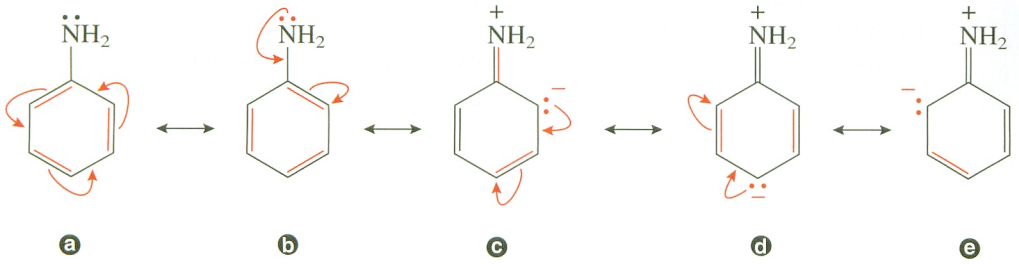
Strategy

Examine the structure and determine the conjugated series of orbitals that is involved in resonance. Next, determine the types of resonance interactions that are present (see Figures 3.16–3.20). Draw the resonance structures and evaluate their relative stabilities

using the octet rule and the number and location of any formal charges. More stable resonance structures contribute more to the resonance hybrid, and structures of equal stability make equal contributions. If the molecule has several important resonance structures, then it has a large resonance stabilization. If, on the other hand, one of the resonance structures is considerably more stable than the others, then the molecule looks very much like this structure and its energy is close to that of this structure—it has only a small resonance stabilization.

Solution

The nitrogen is sp^2 hybridized with its "unshared" pair of electrons in a p orbital. This is a combination of the resonance types involving a cycle of double bonds and a pair of electrons next to a double bond. In fact, the situation is very similar to that shown for the anion derived from phenol in Figure 3.21. The important resonance structures are as follows:



Structures **a** and **b** are equivalent and make identical contributions to the resonance hybrid. Because of their formal charges, structures **c**, **d**, and **e** make lesser contributions. Overall, this compound has considerable resonance stabilization.

PROBLEM 3.17

Draw the important resonance structures for these species. Use the curved arrow convention to show how the electrons are moved to create each new resonance structure. Discuss the relative contribution of each to the resonance hybrid and the overall resonance stabilization of the species.

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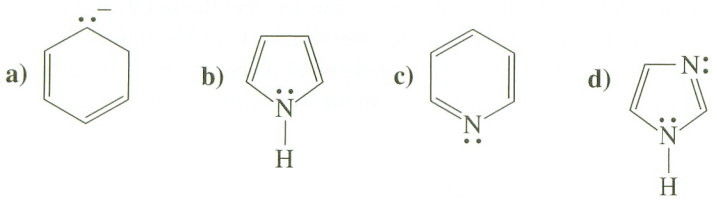
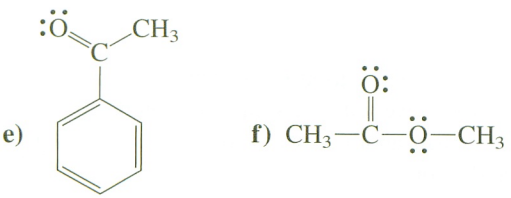
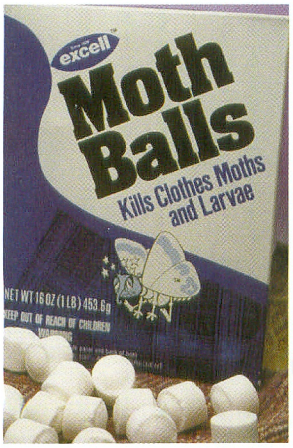




Focus On



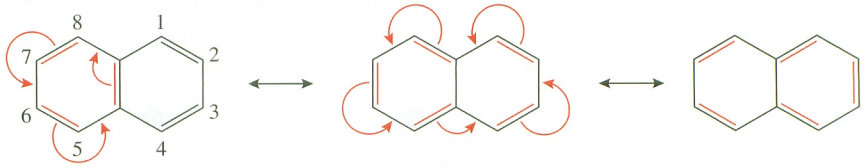
Charles D. Winters

Moth balls are made from napthalene.

Resonance and the Bond Lengths of Naphthalene

Figure 3.20 shows that there are two equivalent resonance structures for benzene. Each has alternating double and single bonds around the ring, so a particular carbon–carbon bond is a single bond in one structure and a double bond in the other. Because both structures contribute equally to the resonance hybrid, all the carbon–carbon bonds of benzene are identical and are intermediate in length between single and double bonds. A typical carbon–carbon single bond has a length of 1.54 Å, and a double bond has a length of 1.34 Å. The carbon–carbon bond lengths of benzene are 1.40 Å, intermediate between those of a single bond and a double bond, as predicted.

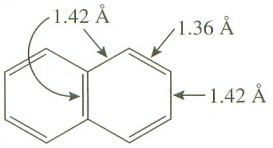
Naphthalene, which has two benzene-type rings fused together, provides a more interesting test for the predictive powers of resonance theory. There are three resonance structures for naphthalene, each with alternating single and double bonds around the rings:



Naphthalene

Although the structure on the left differs slightly from the other two, which are equivalent, all three are quite similar and are expected to make nearly equal contributions to the resonance hybrid.

Now let's examine each bond in the different resonance structures. The bond between C-1 and C-2 is double in two of the resonance structures and single in only one. The same is true for the other bonds that are equivalent to this one, those between C-3 and C-4, between C-5 and C-6, and between C-7 and C-8. All of the other bonds are double in one resonance structure and single in two. Therefore, we would predict that the bond between C-1 and C-2, and the other equivalent bonds, should be shorter than the bonds in benzene but still longer than a normal double bond. The other bonds should be longer than the bonds in benzene but still shorter than a normal single bond. These predictions agree with the experimental bond lengths, which are shown in the following structure:



This is just one example of how resonance can be used to explain or predict experimental observations. In subsequent chapters we will use similar reasoning to explain why one compound is more reactive than another, why a particular site in a molecule is more reactive than another, and so on.

3.9 Molecular Orbital Energies

Section 3.2 explained that two molecular orbitals are formed when two atomic orbitals overlap. One of these MOs is lower in energy than the interacting AOs (a bonding MO), and the other is higher in energy than the AOs (an antibonding MO). Although this model, which uses localized MOs, is only an approximation for molecules with more than two atoms, it is adequate for most situations. Using this model, let's now see how the energies of the MOs are arranged for some larger molecules.

In general, the lowest-energy MOs are sigma bonding MOs. They are low in energy because good overlap between the AOs causes ΔE to be large. For this same reason, sigma antibonding MOs are usually the highest-energy orbitals. Pi bonding MOs are not as low in energy as sigma bonding MOs because the overlap of the p atomic orbitals is not as good in the pi bonds, resulting in a smaller ΔE. For similar reasons, pi antibonding MOs are not as high in energy as sigma antibonding MOs. Finally, nonbonding orbitals, being neither bonding nor antibonding, are between the bonding and antibonding MOs in energy.

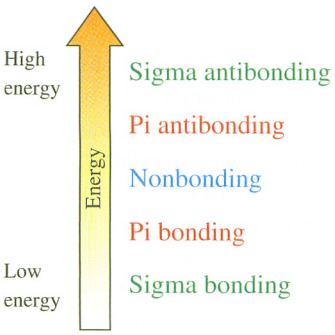


Figure 3.23 is a MO energy level diagram for ethane. This molecule has six CH bonds and one CC bond, so there are seven σ bonding MOs and the corresponding antibonding MOs. Although different sigma bonding MOs (or antibonding MOs) have different energies, these differences are usually not important to us. Therefore, the MO energy level diagrams in this book show all of these MOs at the same energy.

The Lewis structure for ethane shows that there are 14 electrons in this molecule. When these 14 electrons are placed in the MO diagram according to the same rules that

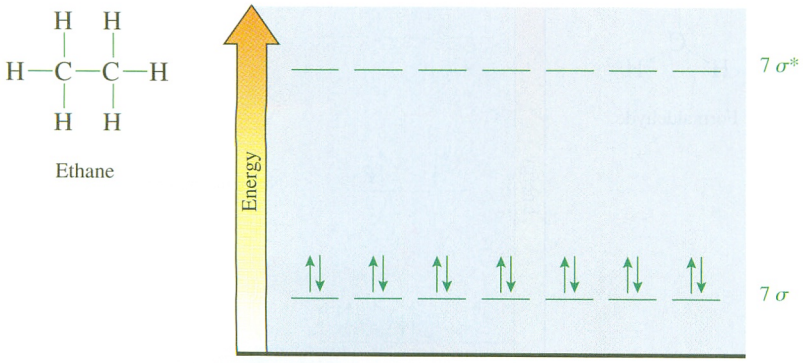
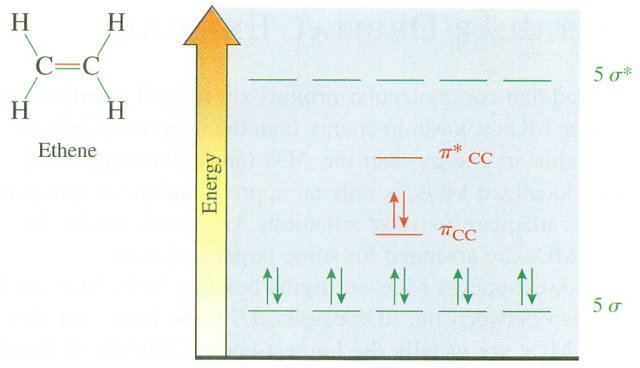


Figure 3.23

MOLECULAR ORBITAL ENERGY LEVEL DIAGRAM FOR ETHANE, C_2H_6.

Figure 3.24

MOLECULAR ORBITAL ENERGY LEVEL DIAGRAM FOR ETHENE, C_2H_4.



were used previously, the bonding MOs are all filled with electrons and the antibonding MOs are empty. This is typically what happens when an MO energy level diagram is constructed: the bonding MOs are filled, and the antibonding MOs are empty. This is the lowest-energy arrangement of the electrons and is termed the *ground electronic state* for the molecule. Any other arrangement of electrons is less stable and is termed an *excited electronic state.*

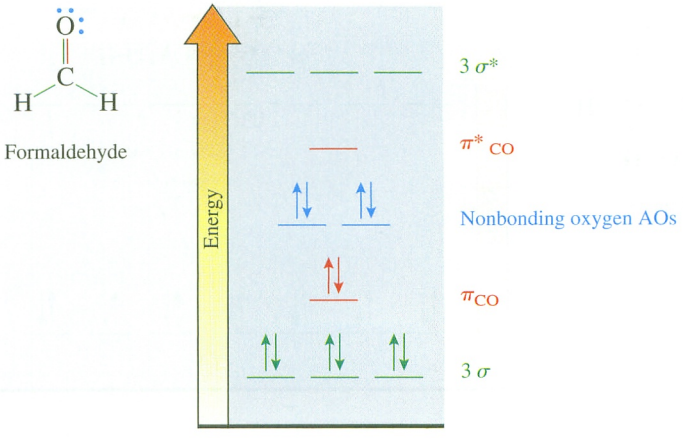
Figure 3.24 shows a MO energy level diagram for ethene. This molecule has four CH sigma bonds, one CC sigma bond, and one CC pi bond. There is a bonding MO and an antibonding MO for each of these bonds. The diagram shows the sigma MOs at the same energy. However, the pi bonding MO is significantly higher in energy than the sigma bonding MOs, and the pi antibonding MO is significantly lower in energy than the sigma antibonding MOs. The Lewis structure shows that there are 12 electrons to place in these MOs. Again, the bonding MOs are filled, and the antibonding MOs are empty.

Figure 3.25 shows a similar diagram for formaldehyde. The difference here is the presence of two unshared pairs of electrons on the oxygen. These electrons are in oxygen nonbonding AOs. The nonbonding orbitals are approximately in the middle of the energy level diagram. This time there are 12 electrons in the orbitals. The bonding and nonbonding orbitals are filled, and the antibonding orbitals are empty.

Diagrams similar to Figures 3.23, 3.24, and 3.25 will apply to most of the molecules that are encountered in this text. When delocalized MOs are discussed in Chapters 16 and 22, some modifications to the energy levels of the pi MOs will be necessary. However, these pi MOs will still remain between the sigma bonding and sigma antibonding MOs in energy.

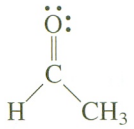
Figure 3.25

MOLECULAR ORBITAL ENERGY LEVELS FOR FORMALDEHYDE, CH_2O.



PROBLEM 3.18
Show energy level diagrams for the MOs of these compounds.

a) H—C≡N:

b) 

c) $CH_3—\ddot{N}H_2$

Review of Mastery Goals

After completing this chapter, you should be able to:

- Assign the ground-state electron configuration for simple atoms.
- Identify any bond as sigma or pi. (Problem 3.34)
- Draw pictures for various sigma and pi bonding and antibonding MOs.
- Identify the hybridization of all atoms of a molecule. (Problems 3.20, 3.21, 3.22, 3.40, and 3.44)
- Identify the type of molecular orbital occupied by each electron pair in a molecule and designate the atomic orbitals that overlap to form that MO. (Problems 3.21 and 3.40)
- Draw the important resonance structures for any molecule. Assign the relative importance of these structures and estimate the resonance stabilization energy for the molecule. (Problems 3.24, 3.25, 3.26, 3.27, 3.28, 3.29, 3.35, 3.36, 3.37, 3.38, and 3.41)
- Show a MO energy level diagram for all the orbitals for any molecule. (Problems 3.30, 3.31, 3.32, 3.33, and 3.39)

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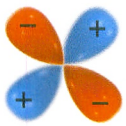
Click *Mastery Goal Quiz* to test how well you have met these goals.

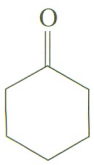
Additional Problems

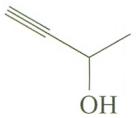
3.19 Show the location of the two planar nodes in this 3*d* atomic orbital:

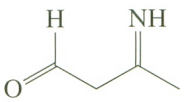


3.20 What is the hybridization at all atoms, except hydrogens, in these compounds?

a) $CH_3—NH_2$ b) $CH_2=CHCH_2C\equiv N$ c)

d) 

e) 

f) 

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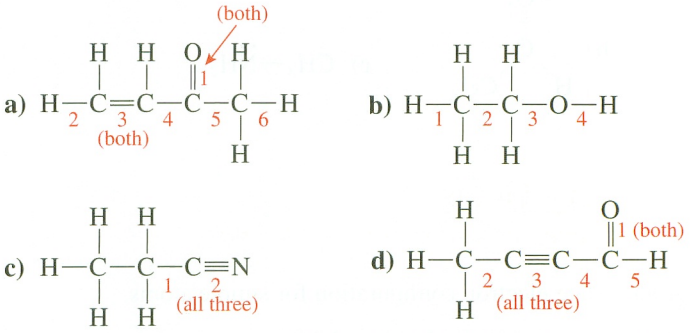
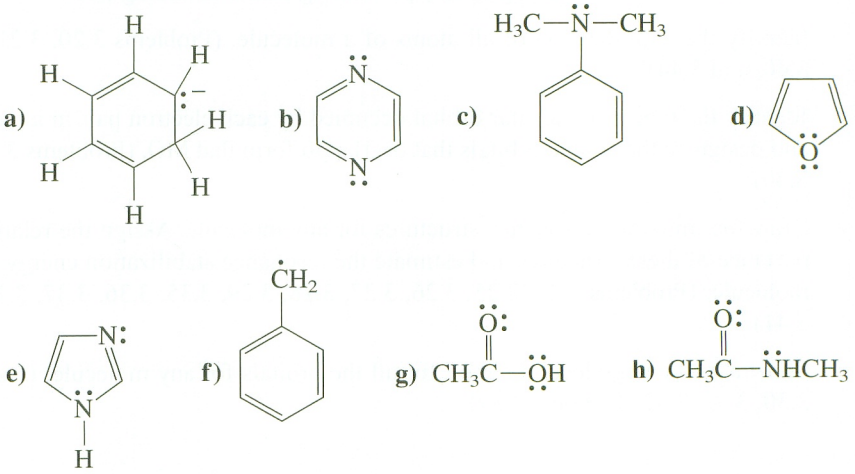
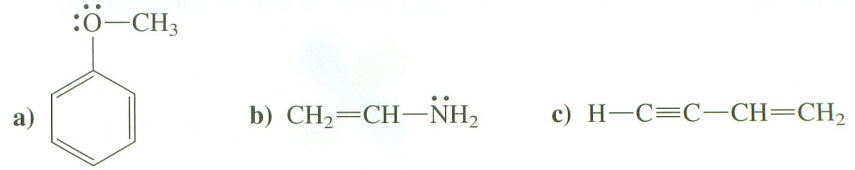
3.21 Show the hybridization at each of the atoms, except H, in these molecules. Indicate the type of each designated bond and the orbitals that are overlapping to form it.



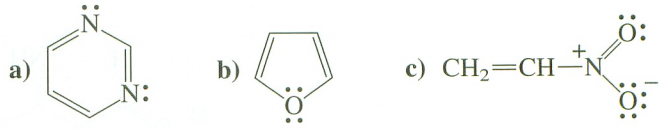
3.22 What is the hybridization at all atoms, except hydrogens, in these compounds?

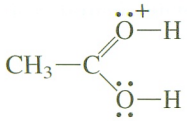


3.23 Draw the *p* orbitals that compose the conjugated part of these molecules:



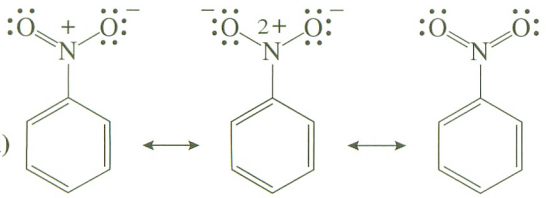
3.24 Show the important resonance structures for these compounds. Use the curved arrow convention to show how the electrons are moved to create each new resonance structure.

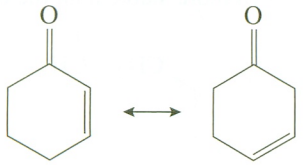


d) 

e)

3.25 In these examples the additional structure or structures are not important contributors to the resonance hybrid for the compound represented by the first structure. Explain.

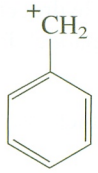
a) 

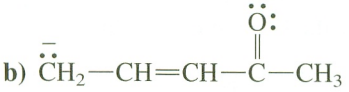
b) 

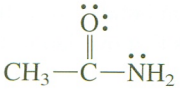
c)

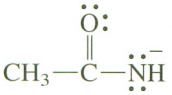
d)

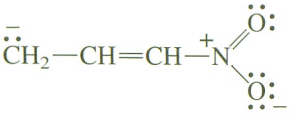
3.26 Draw the important resonance structures for these species and discuss the contribution of each to the resonance hybrid. Explain whether the species has a large or a small amount of resonance stabilization.

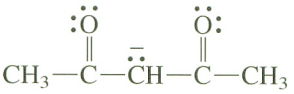
a) 

b) 

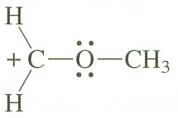
c) 

d) 

e) 

f) 

3.27 Explain why this carbocation is considerably more stable than this structure would suggest:

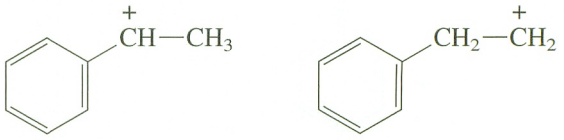


3.28 Explain why one of these anions is much more stable than the other:

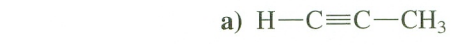
a)

b)

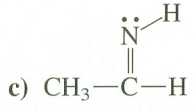
3.29 Explain why one of these carbocations is much more stable than the other:



3.30 Show energy level diagrams for the MOs of these compounds:

a) 

b)

c) 

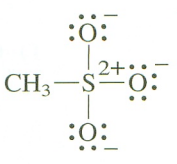
3.31 The energy level diagram for the MOs of $CH_2{=}CH_2$ is shown in Figure 3.24. Show a similar diagram for the lowest-energy excited state of this molecule.

3.32 Consider the species formed by the addition of an extra electron to H_2 so that there are three electrons and a negative charge. Show an energy level diagram for the MOs of this species. Is there still a bond between the hydrogens—that is, is it still necessary to add energy to cause the atoms to separate? Predict how the bond length of this species compares to that of H_2.

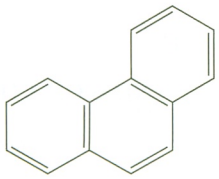
3.33 Draw an energy level diagram for the excited state of H_2. Is there still a bond between the hydrogens?

3.34 Consider $H_2C{=}C{=}CH_2$. What is the hybridization and geometry at each C? Indicate the bond types for each of the carbon–carbon bonds. Draw the molecule, showing the overall geometry and the *p* orbitals that overlap to form the pi bonds. (The molecule is not planar.) Is it conjugated?

3.35 Draw resonance structures for this anion. Remember, sulfur can have 10 or even 12 electrons in its valence shell.

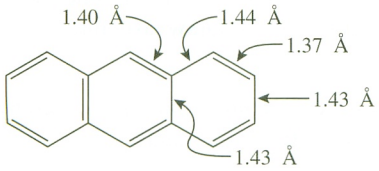


3.36 Phenanthrene has five total resonance structures. One is shown here. Draw the other four. Which carbon–carbon bond of phenanthrene would you predict to be the shortest?



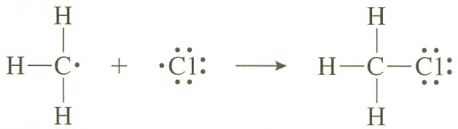
Phenanthrene

3.37 Show the three additional resonance structures for anthracene. Discuss whether the experimental bond lengths shown in the following structure are in accord with predictions based on these resonance structures:



Anthracene

3.38 One general reaction of radicals is the coupling of one with another to form a bond, as shown in the following equation:

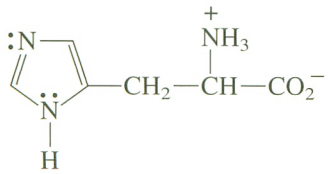


The following coupling reaction gives two products. Show the structures of these products and explain why both are formed.

3.39 Show a MO energy level diagram for the neutral molecule HeH. Use this diagram to explain whether HeH is expected to be stable or not.

3.40 What is the hybridization at each nitrogen of the amino acid histidine? What kind of orbital is occupied by the unshared pair of electrons on each nitrogen? Explain.

BioLink



BioLink

3.41 At a pH of 10.8, the amino acid arginine exists primarily as the following dipolar ion. Show the resonance structures for the cationic part of arginine and discuss their relative contributions to the resonance hybrid.

Arginine

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3.42 Indicate the hybridization at each atom, other than hydrogen, in the compounds represented by these models. Draw structures for each compound represented by the models.

3.43 Draw structures for each compound represented by these models and indicate the conjugated part of the compounds.

3.44 Draw all the important resonance structures for the compounds represented by these models.

3.45 Draw a structure for the neutral molecule represented by the following model. Explain whether the octet rule is satisfied at each atom of the compound. Draw all of the important resonance structures for this molecule.

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